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Proceedings of the Sixth Annual Thermal and Chemical Storage Contractors' Review Meeting

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September 14—16, 1981
Washington, D.C.

Prepared for:
U.S. Department of Energy
Assistant Secretary,
Conservation and Renewable Energy
Division of Energy Storage
Under Contract No. W-7405-ENG-26

Published February , 1982

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Conf-810940

Proceedings of the Sixth Annual Thermal and Chemical Storage Contractors' Review Meeting

September 14—16, 1981
Washington, D.C.

Prepared by:
MCC Associates, Inc.
Silver Spring, Md. 20910

For:
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830
Under Contract No. W-7405-ENG-26

Prepared for:
U.S. Department of Energy
Assistant Secretary,
Conservation and Renewable Energy
Division of Energy Storage
Washington, D.C. 20585

Published February, 1982

PREFACE

The Department of Energy (DOE), Office of Energy Systems Research (ESR), is engaged in developing and disseminating thermal and thermochemical energy storage technology as a means of achieving the efficient and reliable utilization of alternative energy sources such as solar and other intermittent sources, industrial waste heat for internal or external applications, and utility base load generation capacity (off-peak electricity). This component of the National energy storage program is composed of four subprograms, each of which is managed at the National Laboratory level:

- Chemical and Hydrogen Energy Systems -- Brookhaven National Laboratory (BNL)
- Thermal Energy Storage for Building Heating and Cooling, and for Industrial Applications -- Oak Ridge National Laboratory (ORNL)
- Thermal Energy Storage for Solar Thermal Applications -- Sandia National Laboratory at Livermore (SNLL)
- Research & Development, and Analysis & Assessments -- Solar Energy Research Institute (SERI)

Other storage technologies such as batteries and electrochemical cells, mechanical and magnetic devices, and underground concepts, are also under development by the DOE, but they are the subject of other Proceedings.

Because of the dispersed program management and the magnitude of the thermal and chemical energy storage effort, annual reviews are held to assess the subprograms and individual projects (subcontractors), and to provide overall guidance and perspective. Attendance is limited to program participants (subcontractors), government sponsors and users, and National Laboratory management personnel. However, the information presented at these meetings is widely disseminated through publication of the proceedings.

The Thermal and Chemical Energy Storage program was formed in late 1975. Proceedings of the first annual review meeting, which was held at the NASA-Lewis Research Center in September 1976, were not published because the program was still largely in its formative stage and the results limited. Proceedings of all subsequent annual reviews have been published as follows:

- Proceedings of the Second Annual Thermal Energy Storage Contractors' Information Exchange Meeting, Sept. 29-30, 1977, Gatlinburg, TN, CONF-770955
- Proceedings of the DOE Chemical/Hydrogen Energy Systems Contractor Review, Nov. 16-17, 1977, Hunt Valley, MD, CONF-771131
- Proceedings of the DOE Chemical/Hydrogen Energy Systems Contractor Review, Nov. 27-30, 1978, Washington D.C., CONF-781142
- Third Annual Proceedings of Thermal Energy Storage Contractors' Information Exchange Meeting, Dec. 5-6, 1978, Springfield, VA, CONF-781231
- Proceedings of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, Nov. 13-14, 1979, Reston, VA, CONF-791127
- Thermal Energy Storage -- Fourth Annual Review Meeting, Dec. 3-4, 1979, Tysons Corner, VA, CONF-791232
- Proceedings of the DOE Thermal and Chemical Storage Annual Contractors' Review Meeting, Oct. 14-16, 1980, McLean, VA, CONF-801055

All proceedings are organized in terms of each of the subprogram areas, with an overview by each responsible subprogram manager leading off that section.

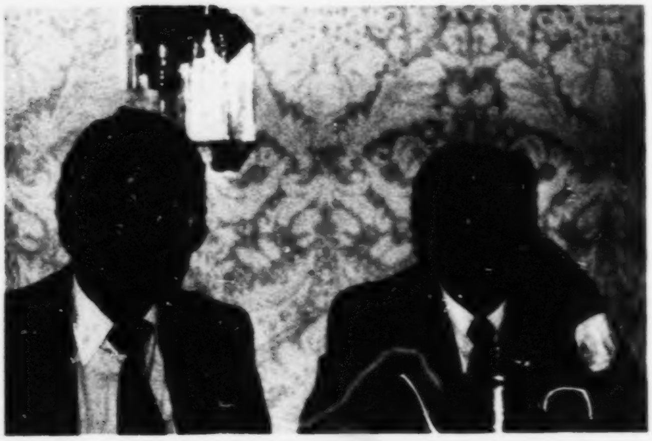
This proceedings volume for the Annual Mechanical, Magnetic and Underground Energy Storage Review Meeting contains the program overviews and contractor summaries and reports presented at the meetings. The summaries and reports were prepared by the responsible individuals/organizations. No technical editing or evaluation has been performed by Los Alamos National Laboratory or the Department of Energy.

John D. Rogers, LANL	James H. Swisher
Conference Chairman,	Director, Division of Energy Storage Technology

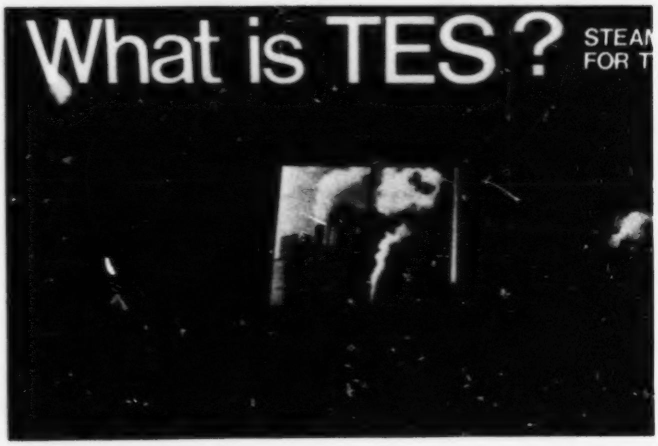
Dr. James H. Swisher, DOE Conference Chairman, greets banquet speaker Dr. Ezra Heitowit. Dr. Heitowit represented the U.S. House of Representatives Subcommittee on Science and Technology.

Pamela S. Moritz of TRW presents a paper on "Chemical Heatpump Cost Effectiveness Evaluation."

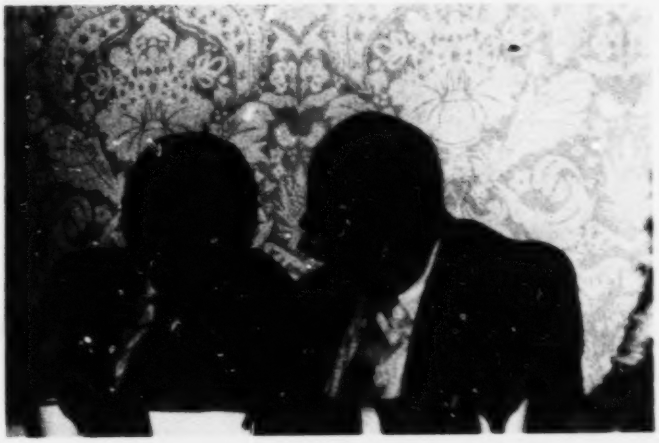
Dr. Allan I. Michaels (Argonne) discusses Calvin MacCracken's (Calmac) poster presentation on "Modular Ice-Storage Tank/Heat Exchangers."



Dr. Michael Gurevich and Saul Strauch of DOE's Division of Physical and Chemical Energy Storage attend the banquet.



A segment of the poster display presented by Howard Edde of Bellevue, Washington.



Conference Chairman James Martin (ORNL) discusses procedures with Alessio Mezzina (BNL)

PROCEEDINGS OF THE DEPARTMENT OF ENERGY'S SIXTH THERMAL AND CHEMICAL STORAGE ANNUAL CONTRACTORS' REVIEW MEETING

PREFACE i

PHOTOGRAPHS iii

TABLE OF CONTENTS v

TABLE OF CONTENTS

CHEMICAL/HYDROGEN ENERGY SYSTEMS

BROOKHAVEN NATIONAL LABORATORY CHEMICAL/HYDROGEN ENERGY SYSTEMS PROGRAM OVERVIEW
Alessio Mezzina (Brookhaven National Laboratory) 3

HYDROGEN PRODUCTION (Electrolytic)

STATUS OF THE DEVELOPMENT OF SOLID POLYMER ELECTROLYTE WATER ELECTROLYSIS FOR LARGE SCALE HYDROGEN GENERATION
John H. Russell (General Electric Company 11

ADVANCED ALKALINE WATER ELECTROLYSIS
John N. Murray (Teledyne Energy Systems) 16

STATIC FEED WATER ELECTROLYSIS FOR LARGE SCALE HYDROGEN GENERATION
F. H. Schubert and K. A. Burke (Life Systems, Inc.) 21

SELECTION AND EVALUATION OF MATERIALS FOR ELECTROCHEMICAL ENERGY CONVERSION DEVICES: ELECTROCHEMICAL EVALUATION OF NICKEL WHISKER ELECTRODES
J. D. Hansen, G. E. Stoner, G. L. Cahen, Jr., and L. L. Scribner
(University of Virginia) 29

RESEARCH ON ADVANCED ELECTROLYTIC HYDROGEN PRODUCTION (Thermochemical)
H. S. Isaacs, C. Y. Yang, and J. McBreen (Brookhaven National Laboratory) 35

HYDROGEN PRODUCTION (Thermochemical)

THE SULFUR-IODINE THERMOCHEMICAL WATER-SPLITTING CYCLE
G. E. Besenbruch, J. H. Norman, C. L. Allen, L. C. Brown, D. R. O'Keefe,
M. L. Kelly, M. Yoshimoto, M. Endo, and P. W. Trester (General Atomic Co.) 43

ALTERNATE THERMOCHEMICAL CYCLES
Charles M. Hollabaugh, Melvin G. Bowman, and Charles L. Peterson
(Los Alamos National Laboratory) 47

SOLUBILITY OF SULFUR DIOXIDE IN SULFURIC ACID
Karl K. Chang, Leslie E. Compton and Daniel D. Lawson (Jet Propulsion Laboratory) . . 52

HYDROGEN STORAGE/RECOVERY

HYDROGEN COMPATIBILITY OF STEELS
J. H. Holbrook, H. J. Cialone, and M. E. Mayfield (Battelle/Columbus) 59

METAL HYDRIDE PROCESS FOR HYDROGEN RECOVERY
E. Lee Huston (MPD Technology Corp/Ergenics Division) 63

RECOVERY OF HYDROGEN FROM HYDROGEN SULFIDE
Gopala N. Krishnan and Donald L. Hildenbrand (SRI International) 70

SYSTEMS ANALYSIS OF H_2/NATURAL GAS SUPPLEMENTATION AND SEPARATION
M. Beller and J. D'Acierno (Brookhaven National Laboratory) 75

HYDROGEN RECOVERY FROM SUPPLEMENTED NATURAL GAS BY METAL HYDRIDES
D. T.-J. Huang, F. Reidinger, and F. B. Hill (Brookhaven National Laboratory) 81

CHEMICAL HEATPUMP

SULFURIC ACID/WATER CHEMICAL HEATPUMP ENERGY STORAGE PROGRAM
E. C. Clark (Rocket Research Company) 91

CHEMICAL HEAT PUMP COST EFFECTIVENESS EVALUATION
Warren R. Standley (TRW Energy Engineering Division) 98

METAL HYDRIDE/CHEMICAL HEAT PUMP DEVELOPMENT PROJECT
Hector A. Madariaga (Southern California Gas Company)
David A. Rohy (Solar Turbines Inc.) 106

METAL-HYDRIDE HEAT-PUMP PERFORMANCE STUDIES
H. I. Abelson and J. M. Clinch (Argonne National Laboratory) 114

TES FOR BUILDING HEATING & COOLING

OAK RIDGE NATIONAL LABORATORY THERMAL ENERGY STORAGE PROGRAM OVERVIEW
James F. Martin (Oak Ridge National Laboratory) .125

TES/HEAT PUMP PERFORMANCE EVALUATION
T. W. Sigmon, J. H. Davidson, and D. H. Abbott (Research Triangle Institute) 131

RESIDENTIAL SCALE ICE STORAGE SYSTEM FOR SPACE COOLING
Harold H. Hopkinson (Carrier Corporation) 137

EVALUATION OF OLIVINE REFRACTORIES FOR TES
B. M. Gay, H. Palmour III, R. L. Cochrane, and M. J. Paisley
(North Carolina State University) 141

ALTERNATIVES TO CERAMIC BRICKS AND CERAMIC BRICK SYSTEMS
Michael MacDonald and David Goldenberg (TRW/Energy Development Group) 147

THERMAL ENERGY STORAGE TESTING FACILITY
R. J. Schoenhals, S. H. Anderson, L. W. Stevens, W. R. Laster and M. R. Elter
(Purdue University) 155

FIELD EVALUATION AND ASSESSMENT OF THERMAL ENERGY STORAGE FOR RESIDENTIAL SPACE HEATING: AN INTERIM REPORT
Herb Hersh (Argonne National Laboratory) 161

ASSESSMENT OF COOL STORAGE IN COMMERCIAL BUILDING APPLICATIONS
J. G. Asbury, J. M. Calm, and R. F. Giese (Argonne National Laboratory) 166

PELLETIZATION AND ROLL ENCAPSULATION OF PHASE CHANGE MATERIALS
Johnson Chen, Robert Nelson, and F. X. Polinski (Pennwalt Corporation) 176

EFFECT OF ADDITIVES ON PERFORMANCE OF HYDRATED SALT TES SYSTEMS
Calvin D. MacCracken (Calmac Manufacturing Corporation) 185

DEVELOPMENT OF ADVANCED BUILDING MATERIALS FOR THE PASSIVE SOLAR APPLICATION
John J. Tomlinson (Oak Ridge National Laboratory) 189

ASSESSMENT OF ENERGY STORAGE FOR SOLAR APPLICATIONS
David J. Edwards and Solomon Rosenzweig (The Aerospace Corporation) 193

MODELING HEAT TRANSFER IN PCM'S WITH THE BUDAK METHOD
Ralph M. Deal and Jo Ann Millard (Kalamazoo College) 201

SURVEY OF COMMERCIAL THERMAL STORAGE INSTALLATIONS IN THE UNITED STATES AND CANADA
Harold G. Lorsch and Michael A. Baker (Franklin Research Center) 205

PERFORMANCE OF LABYRINTH-STRATIFIED WATER STORAGE SYSTEM FOR HEATING AND COOLING
M. W. Wildin (The University of New Mexico) 211

PERFORMANCE OF STRATIFIED THERMAL STORAGE SYSTEM FOR OLIVER SPRINGS ELEMENTARY SCHOOL: PROGRESS REPORT
R. L. Reid and A. F. G. Bedinger (University of Tennessee) 219

DEVELOPMENT OF NATURAL STRATIFICATION TECHNOLOGY
Roger L. Cole and Frank O. Bellinger (Argonne National Laboratory) 223

ORNL THERMAL ENERGY STORAGE PROGRAM - TECHNICAL SUPPORT
Ralph N. McGill (Oak Ridge National Laboratory) 231

MATHEMATICAL MODELING OF TES SUBSYSTEMS
Alan Solomon (Union Carbide Corporation) 238

TES FOR INDUSTRIAL APPLICATIONS

APPLICATION OF THERMAL ENERGY STORAGE TO PROCESS HEAT RECOVERY, PHASE III, HEAT EXCHANGER EVALUATION
L. B. Katter (Rocket Research Company) 245

BELLINGHAM PHASE III
Gerard L. Vanroyen, Jake E. Collins, and Mary A. McGee
(Trans Energy Systems, Inc.) 249

TES TECHNOLOGY TRANSFER IN THE PULP AND PAPER INDUSTRY
Howard Edde and Jay Handley (Howard Edde, Inc.) 256

ADVANCED HIGH-TEMPERATURE THERMAL ENERGY STORAGE MEDIA FOR INDUSTRIAL APPLICATIONS
T. D. Claar and R. T. Waibel (Institute of Gas Technology) 262

SANDIA NATIONAL LABORATORY SOLAR THERMAL APPLICATIONS

MOLTEN NITRATE SALT STUDIES FOR CENTRAL RECEIVER APPLICATIONS
S. H. Goods and R. W. Mar (Sandia National Laboratories) 271

MOLTEN SALT THERMAL ENERGY STORAGE SUBSYSTEM FOR SOLAR THERMAL CENTRAL RECEIVER PLANTS
Philip B. Wells (Martin Marietta Denver Aerospace)
George P. Nassopoulos (American Technigaz, Inc.) 278

THERMAL CONDUCTIVITY OF MOLTEN ALKALI NITRATES
Bjorn Hafskjold and Harold A. Oye (Norwegian Institute of Technology) 286

CORROSION BEHAVIOR OF ALLOYS
Hector Fernandez and R. A. Osteryoung (State University of New York) 294

EFFECTS ON SOILS FROM HOT STORAGE TANKS
Kenneth C. Ko (Kenneth C. Ko & Associates, Inc.) 301

CONCEPTUAL DESIGN OF THE MOVING BED THERMAL ENERGY STORAGE SYSTEM FOR A COMMERCIAL SCALE (100 MWe) SOLAR CENTRAL RECEIVER POWER PLANT
R. L. Wright, T. P. Suchocki, and D. C. Schluderberg (Babcock & Wilcox Company) . . .308

CONCEPTUAL DESIGN OF A LATENT HEAT THERMAL ENERGY STORAGE SUBSYSTEM FOR A SATURATED STEAM SOLAR RECEIVER AND LOAD
Gerald F. di Lauro (Combustion Engineering, Inc.)
Richard E. Rice (Comstock and Wescott, Inc.) 317

SINGLE MEDIA THERMOCLINE TES STUDIES AT SANDIA NATIONAL LABORATORIES
Robert J. Gross (Sandia National Laboratories) 323

DISH-MOUNTED LATENT HEAT BUFFER STORAGE
Ram Manvi (Jet Propulsion Laboratory) 330

APPLICATION OF BUFFER THERMAL ENERGY STORAGE TO AN AIR BRAYTON SOLAR ENGINE
Hal J. Strumpf and Kevin P. Barr (AiResearch Manufacturing) 340

SERI - RESEARCH DEVELOPMENT AND ANALYSIS & ASSESSMENTS

THE SERI SOLAR ENERGY STORAGE PROGRAM
Charles E. Wyman (Solar Energy Research Institute) 353

COST AND PERFORMANCE OF THERMAL STORAGE CONCEPTS IN SOLAR THERMAL SYSTEMS
A. W. McKenzie (Stearns-Roger Services Inc.) 359

SYSTEMS ANALYSIS OF THERMAL STORAGE
R. J. Copeland (Solar Energy Research Institute) 365

THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT
R. Gerald Nix (Solar Energy Research Institute) .372

HIGH TEMPERATURE ACTIVE HEAT EXCHANGER RESEARCH FOR LATENT HEAT STORAGE
Joseph Alario and R. Haslett (Grumman Aerospace Corp) 376

HIGH TEMPERATURE INTEGRATED THERMAL STORAGE FOR SOLAR THERMAL APPLICATIONS
Adam P. Bruckner and Abraham Hertzberg (University of Washington)
Robert T. Taussig (Mathematical Sciences Northwest) 383

HIGH-TEMPERATURE COMPOSITE LATENT/SENSIBLE HEAT STORAGE
T. D. Claar and R. J. Petri (Institute of Gas Technology) 390

THERMAL AND CHEMICAL STORAGE ANNUAL CONTRACTORS' REVIEW MEETING - AGENDA 396

LIST OF ATTENDEES 401

CHEMICAL/HYDROGEN ENERGY SYSTEMS

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2

BROOKHAVEN NATIONAL LABORATORY
CHEMICAL/HYDROGEN ENERGY SYSTEMS
PROGRAM OVERVIEW

Alessio Mezzina
Brookhaven National Laboratory
Upton, New York 11973

1.0 INTRODUCTION

Brookhaven National Laboratory (BNL) provides management, technical oversight, and in-house R&D support to the C/HES Program on behalf of the Division of Energy Storage in the DOE Office of Energy Systems Research. Through FY 81 the program elements have addressed: Hydrogen Production; Storage Systems and Materials; Chemical Heat Pumps and Chemical Energy Systems. Recent policy and budgetary guidance will be reflected in redirection of the BNL programmatic thrust in FY 82. Emphasis will be shifted from near- to mid-term systems development and commercialization toward more fundamental and exploratory activities. Technology upgrade and application will look to the longer-term prospects for penetration of the energy infrastructure.

The shifts in direction and emphasis will draw more heavily upon a broad range of scientific and engineering disciplines from academe and the national laboratories. As opposed to the systems development support nature in the recent past, technology research and exploratory investigations will drive future private sector activity by addressing technological advances considered as high risk by the industrial and commercial communities yet offering high payoff.

Consistent with new policy guidance, projects will be formulated in areas of technology such as energy conversion and storage, energy and materials management and resource recovery. The objectives will aim toward the delivery of technology packages which will clearly identify the technical and economic risks associated with future systems development, process or systems scale-up and ultimate commercialization by the private sector.

2.0 PROGRAM DESCRIPTION AND OVERVIEW

The C/HES Program was impacted substantially by FY 81 rescissions and revised policy guidance. The Hydrogen Technology Program element in particular has undergone major redirection.

2.1 Current Status

FY 81 status and highlights are summarized for each of the major activities:

Hydrogen Production

- The SPE Water Electrolysis Project at GE was curtailed and redirected in February 1981. Pacing problems as pertain to demonstrating operating efficiency >80% with low catalyst loadings were being addressed at the time a "stop work" order was issued. The project continued to indicate uncertainties with respect to meeting cost and performance goals which were further compounded by concerns of life and reliability factors due to potential SPE membrane degradation and high degree of susceptibility to low level impurities in water.

- The Static Feed Water Electrolysis concept pursued at Life Systems, Inc. continues to show promise as a low cost, high efficiency alternative to conventional as well as SPE systems. Modest efforts supported to date indicate the capability of operating at high current densities with brackish water. The system design promises the elimination of parasitic power for operating pumps and water clean-up subsystems and offers greater flexibility for matching power conditioning output at maximum efficiency. These characteristics suggest possible consideration for OTEC plantship applications, but a five-year system development and scale-up program is required.

- Advanced Alkaline Electrolysis component testing at Teledyne Energy Systems indicates that improved electrode, catalyst, and separator systems capable of operating in the 120°C temperature regime can compete with the more realistic projections of SPE electrolyzer cost and performance characterization.

- The Production of Hydrogen from Small Hydropower at NYSERDA/Potsdam has been stopped short of commitment to construction. New PURPA regulations suggest that hydrogen production revenue requirements compared to probable revenues from direct sales of electricity to the local utility will make hydrogen noncompetitive with current market prices for merchant hydrogen.

- Photolytic Water Decomposition studies at BNL have aimed toward the development of low cost, high efficiency heterojunctions. BNL investigations have shown that improved semiconductor heterojunctions can exhibit optimal compromise of (band-gap) response and stability by appropriate preparation of substrates with good response and thin-film overlays with good stability characteristics. Further investigations geared toward optimizing heterojunction fabrication will set the stage for advanced water-splitting systems development. Techniques developed in thin-film deposition may extend to other semiconductor applications.

Hydrogen Storage/Transport

- Microcavity Storage Systems investigated by Robert J. Teitel Associates were found unsuitable for the cost-effective storage of hydrogen in either bulk or mobile storage applications. This conclusion relates to commercial grade material now being marketed. Findings have suggested that "customized" microspheres could provide improved "fill/release" characteristics as well as recyclability to reduce cost.

- Natural Gas Supplementation with hydrogen was reevaluated at BNL. The concept was evaluated also as a hydrogen transport option by considering the possibility of separating the hydrogen at user sites consistent with needs of merchant hydrogen and larger user markets. The study aimed to determine if the separation option would compete with delivery/storage alternatives of a conventional nature. Findings have reinforced the inhibiting influence of diseconomies resulting from price disparities between H_2 and natural gas. The separation/purification incentive can only be pursued if the natural gas is not returned to the network for credit; however, the steel industry offers a strong potential market for direct reduction of iron ore as scrap iron sources become depleted. Economics control the viability of such an application.

- The use of ammonia as a hydrogen transport/storage alternative was examined at BNL. This option had been evaluated for OTEC plantship application but findings have suggested that as electricity prices escalate, storage/transport alternatives to hydrogen liquefaction appear more attractive, independent of the resource converted. Current state-of-the-art technology can be applied to catalytically cracking ammonia and purifying the H_2 for most user applications. Low temperature catalysts and improved purification schemes would enhance the ammonia transport/storage alternative to H_2 liquefaction/dewar storage. The possibilities may extend to use of NH_3-derived H_2 as a fuel alternative in selected user sectors such as in agricultural vehicles and machinery and maritime applications.

Chemical Energy Systems

- Hydrogen Separation/Purification from Industrial Waste Streams is a project under investigation at APCI/Ergenics. Emphasis is being placed on identifying metal hydrides and their poison-resistant characteristics. Such definition will then permit process development and designs including stream pre-cleanup in the form of process flow sheets. The DOE-funded effort addresses hydrogen recovery from refinery gases as a major target. A parallel self-sponsored effort has been ongoing at APCI/Ergenics for recovering hydrogen from ammonia process off-gases. This activity has enjoyed a level of success and has progressed to the PDU stage with testing being conducted at an APCI ammonia plant. Spinoffs of findings will apply to the DOE/BNL-sponsored activity. DOE/BNL does not plan to proceed to pilot plant design and operation at an industrial site.

- H_2 Recovery from H_2S investigations at SRI have proceeded successfully with reasonable success by having demonstrated that H_2S bubbled through molten copper results in a high purity ($\sim$99% H_2 product and the molten reactant can be easily recycled. Energy balance evaluation applicable to process designs focusing on sour gas treatment is being considered for the next phase of the project subject to the development of a strong technical and programmatic rationale for future pursuits.

- The H_2SO_4/H_2O Chemical Heat Pump development at Rocket Research Corporation has progressed on schedule. A 150,000 Btu/hr, 10^6Btu storage system is currently undergoing performance verification testing in the industrial chemical heat pump temperature amplification mode of operation. A test option for characterizing the system in the HVAC mode is open, although application in residential/commercial space conditioning is questionable due to cost penalties associated with low system COP for cooling. The system represents a major state-of-the-art upgrade for industrial waste heat management and is being considered for Engineering Evaluation Test of a scaled-up (1,000,000 Btu/hr) system in FY 82 subsequent to successful VTU performance verification at RRC.

- Metal Hydride CHP development at Southern California Gas/Solar Turbine International was initiated in February 1981 following a competitive procurement. Current efforts stress identification of the application and configuration prior to commitment to component and subsystem design development and test. BNL has expressed concern regarding contractors' deferral of material selection and component development activity. The key to metal hydride CHP success is the ability to rapidly cycle metal hydrides at minimal tradeoff of COP due to nonregeneration of sensible heat (for heating mode) or nonrejection of sensible heat in cooling mode. It is uncertain if the project will proceed beyond the first "go no-go" decision point unless viable approaches to solving the key pacing problems are identified.

2.2 FY 82 C/HES Program Description (General)

The C/HES Program at BNL will be structured in accordance with DOE fiscal and policy guidance. Planning actions will be based upon a nominal budget authority of $4M; but due consideration will be given to possible BA reductions of $1M as well as possible increases by as much as $3M if the H_2 technology activity is reintroduced as a "line item" in FY 82.

Value judgments have been reflected in the C/HES Program Annual Operating Plan and are summarized as follows:

- Hydrogen Production Technology development will seek out novel approaches. Past efforts into activities such as GE SPE Electrolysis System, GA Sulfur/Iodine Thermochemical Cycles, and TES Component Testing, will be deemphasized in deference to advanced concepts such as novel approaches to thermochemical water decomposition, anode depolarization, high-temperature electrolysis, photolytic water decomposition and continued pursuits in static feed water electrolysis.

- Resource recovery activities will be restricted to process definition associated with H_2 recovery from H_2S with substantial deemphasis of the gas separation investigations as might apply to H_2 recovery from supplemented natural gas or from refinery gases.

- Hydrogen Storage/Transport options will be reexamined with emphasis placed on high risk/high payoff technology.

- Chemical Heat Pump Development will retain a high programmatic priority carrying through engineering evaluation test of first generation systems. Second generation CHP's will seek out alternative reversible reactions which circumvent limitations identified in the earlier development activity.

- In recognition of budget limitations, milestone schedules will be defined accordingly, stressing evolutionary development of fundamental concepts targetted for long-term application in the U.S. energy system.

- Although systems and process engineering and testing of commercializable technology will defer to private sector involvement, the program will retain the option for conducting small-scale technology demonstrations and peformance verification testing.

3.0 BNL'S MANAGEMENT AND FINANCIAL PERSPECTIVE

3.1 Program Organization

New project directions will emphasize base technology and exploratory developments of innovative concepts which promise step-jump improvements in cost and performance characteristics of components, subsystems, and systems. The program organization and structure will incorporate a technology assessment and planning function which will identify and evaluate R&D targets in terms of:

- Long-term impact on the U.S. energy supply situation
- R&D costs weighed against potential benefits

- Milestone schedules versus needs of the user markets
- Technical, cost/economic, institutional and safety/environmental considerations

The FY 82 Annual Operating Plan was submitted to DOE/STOR in July. It reflects a new Program Organization (Figure 1) which will be more responsive to the directed thrust of the C/HES Program with activities structured along disciplinary lines.

The BNL technical management and oversight perspective which has been applied to subcontracted activities will be extended to BNL in-house R&D efforts. In past years, intellectual and technological resources at BNL were "pooled" to serve as complementary and support functions to contracted private sector pursuits associated with various systems developments. Within the new structure, specific in-house projects will be identified including clearly delineated plans and schedules. Each project will be assigned a separate account number and technical progress versus budget outlays will be evaluated accordingly by the appropriate Area Manager.

3.2 Financial Summary

Program activities for fiscal year 1982 have been classified into three basic areas. These functional classifications are consistent with the program organization (Figure 1) and are a direct result of the FY 1982 merging of the Thermochemical, Electrochemical and Chemical Energy Storage/Chemical Heat Pump activities undertaken during the previous fiscal years. The functional classifications group those activities which are directly involved in assessments, base technology research, and systems development.

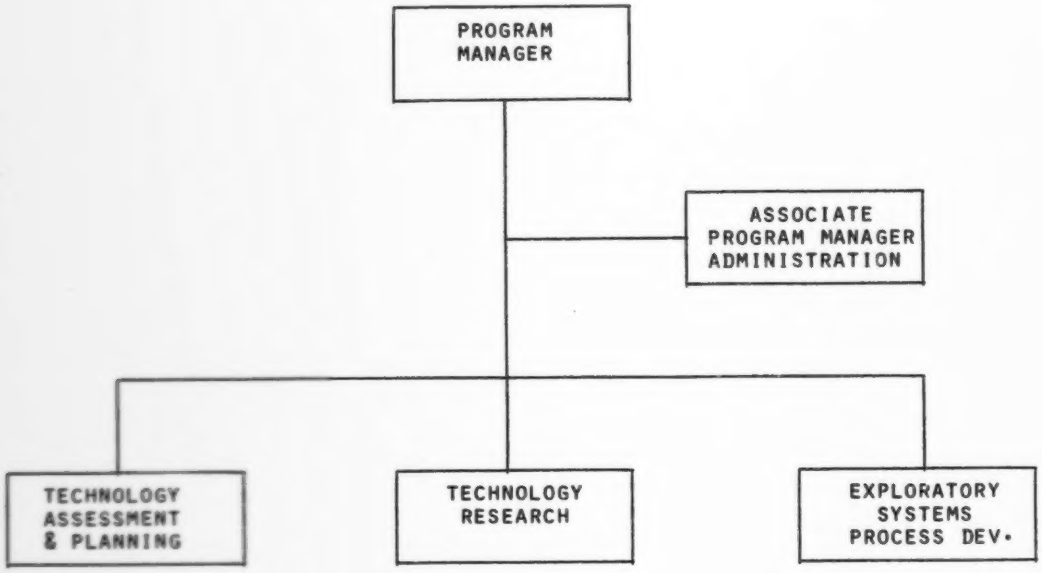
The FY 1982 budget outlay reflects a significant decrease (∿40%) compared to the previous years funding. This funding decrease is compounded further when considered in the context of an inflationary economy. Activities presented in the budget are aimed to be consistent with current administration guidelines and indicate a departure from substantial commitments to demonstration activities towards an increased emphasis on fundamental and exploratory research and development which address long-term high risk/high payoff technologies.

The detailed project budgets (Table 1) represent a rational funding balance between technology planning, research and engineering evaluation.

In addition, certain cost estimates have been included in the budget to provide for bailments, close-outs, etc. which may result during FY 1982 as a result of subcontract terminations.

FIGURE 1

PROGRAM ORGANIZATION


PROGRAM MANAGER
ASSOCIATE PROGRAM MANAGER ADMINISTRATION
TECHNOLOGY ASSESSMENT & PLANNING
TECHNOLOGY RESEARCH
EXPLORATORY SYSTEMS PROCESS DEV.

- PORTFOLIO ANALYSIS
- PROGRAM RATIONALE
- R&D TARGETS EVAL.
- COST/BENEFIT ANALYSIS
- RISK ASSESSMENTS

- ADVANCED ELECTROLYSIS
- HIGH TEMP ELECTROLYSIS
- ALT. MAT./SURFACE SCI.
- ANODE DEPOLARIZATION
- PHOTOLYTIC H_2O DECOMP.
- H_2 EMBRITTLEMENT

- CHEMICAL HEAT PUMPS
- RECOVERY/SEP. PROCESSES
- ADV. TC PROCESSES
- ENERGY MGMT. SYSTEMS
- PV/ELECTROL. INTERFACE

TABLE 1
CHEMICAL/HYDROGEN ENERGY STORAGE
FINANCIAL SUMMARY
31 JULY 81

PROGRAM ACTIVITIES:

		$\$10^3$	
		BA	BO
• Tech Assess. & Planning			
- CHP Sys. Anal.	- TRW	50	50
- Chem. Sys. Anal.	- ERG	50	50
- EETM Field Test	- TBD	150	100
- R&D Portfolio Anal.	- BNL	30	30
- Cost/Benefit Anal. Supp.	- BNL	30	30
- Technology Assess.	- BNL	30	30
		340	290
• Tech. Research			
- Static Feed Water Electrolysis	- LSI	250	150
- Adv. Alk. Sys.	- TES	150	125
- AWE Matl's. Dev.	- U. Va.	0	20
- Adv. T/C (Zeolites)	- TBD	50	50
- H_2 Embrit.	- BMI	150	160
- Adv. H_2 Storage	- TBD	250	125
- Anode Depol.	- BNL	100	100
- Anode Depolarizers Support	- TA&M*	0	0
- Photolytic Water Decomp.	- BNL	100	100
- Photoelectrolysis Support	- BU *	0	0
- Photoelectrolysis	- SUNY*	0	0
		1050	830
• Exploratory Systems Dev.			
- H_2SO_4/H_2O CHP	- RRC	700	450
- MH_x CHP HT/Mass XFER	- TBD	200	180
- Adv. CHP	- TBD	200	180
- Fund. CHP React	- TBD	50	50
- CHP Design Upgrade	- EIC	100	100
- Adv. Process	- GA+	120	90
- Adv. TC Cycles	- LANL	100	100
- H_2S Recovery	- SRI	175	115
- PV/Electrolysis	- BNL	340	340
		1985	1605
• Pgm. Mgt. Tech. Oversight			
- Pgm./Admin. Mgmt.	- BNL	370	370
- ACT/BHO-D.C. Liaison		155	155
- C/HES Mgt. Info	- E:F	0	20
		525	545
• Bailments, Close-outs	- TBD	100	100
	GRAND TOTAL:	4000	3370

*FY 81 SRSA Funding

+May be redirected to high temp. electrolysis work at BNL/Westinghouse

[illegible]

HYDROGEN PRODUCTION (Electrolytic)

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PROJECT SUMMARY

Project Title:	Solid Polymer Electrolyte Water Electrolyzer Technology Development
Principal Investigator:	J.H. Russell
Organization:	General Electric Company Direct Energy Conversion Programs 50 Fordham Road Wilmington, Massachusetts 01887 (617) 657-5277
Project Goals:	The overall objective of this program is to develop low-cost (<$150/kW) hydrogen generation plants (200 kW - 2 MW) for electric utility/industrial chemical applications using the solid polymer electrolyte technology. The goal is to generate hydrogen at high current densities (1000 ASF) at pressures in the range of 100 to 300 psig at an overall efficiency of 85-90%.
Project Status:	Currently under contractual stop-work order due to funding rescission. Techno-economic study and final report in process.
Contract Number:	DE-AC02-78ET26202
Contract Period:	October, 1980 through September, 1981
DOE Funding Level:	$667,000
Funding Source:	Department of Energy and CO-Sponsors

STATUS OF THE DEVELOPMENT OF SOLID POLYMER ELECTROLYTE WATER ELECTROLYSIS FOR LARGE SCALE HYDROGEN GENERATION

J.H. Russell
General Electric Company
Direct Energy Conversion Programs
Wilmington, Massachusetts

ABSTRACT

During GFY 81, progress continued at General Electric in the development of Solid Polymer Electrolyte Water Electrolysis for Large Scale Hydrogen Generation. The joint Department of Energy, Electric Utility and General Electric Company sponsored program was aimed at performance improvement. Reductions in cell impedance were demonstrated which improve cell performance by over 100 mV.

In parallel, an Electric Power Research Institute/Public Service Electric and Gas Program concentrated on developing a prototype 500 SCFH system for field evaluation. This system is currently undergoing system confirmation testing.

INTRODUCTION

The solid polymer electrolyte (SPE) water electrolysis technology development for large-scale hydrogen generation began in 1975 with a design study for Brookhaven National Laboratory (BNL) and has progressed since then under the sponsorship of the Department of Energy (DOE), the New York State Energy Research and Development Authority (NYSERDA), the Niagara Mohawk Power Corporation (NMPC), the Empire State Electric Energy Research Corporation, the Gas Research Institute (GRI), and the General Electric Company.

The general goals of the program are to develop a water electrolysis technology capable of:

- High overall system efficiency: 85-90%
- Low capital cost: $\leq$ \$150/KW (1980 dollars)
- Long life: 40,000 operating hours for the cells and 20 years for the system.

This program, encompassing scale-up to cell sizes of 2.5 and 10 ft^2, has progressed, through GFY 80, to a point where:

- A 2000 SCFH SPE hydrogen generator system containing a 60-cell module of 2.5 ft^2 cells was successfully operated for greater than 700 hours, and
- 10 ft^2 cell and module design had been completed.

During GFY 1981, effort was directed toward performance improvement, primarily in the areas of improved cell sealing, reduced cell impedance, and improved water quality and distribution.

In 1979, a parallel program was started under sponsorship of the Electric Power Research Institute (EPRI) to develop a water electrolysis system for the generation of hydrogen for electric generator cooling. This system utilizes a 1 ft^2 cell appropriate to generation rates in the 100 - 500 SCFH range.

Under this program, during 1981, a prototype 500 SCFH system was assembled under the sponsorship of Public Service Electric and Gas (PSE&G) of New Jersey and is currently undergoing extensive in-house testing prior to field evaluation.

PERFORMANCE IMPROVEMENT

Sealing

During GFY 81, modifications to the cell sealing configuring were made incorporating increased collector sealing ridge height and silicone adhesive Teflon tape on the hydrogen side. Improved sealing with this configuration has been proven on modules containing 6 - 2.5 ft^2 cells, and up to 20 1 ft^2 cells.

Improved Water Purity

Increased cation deionizer capacity downstream of the mixed bed deionizer was found to be very effective in trapping any amines resulting degradation of the anion beads in the mixed deionizer.

Improved Water Distribution

In past 2.5 ft^2 modules, several local areas of membrane attack resulted from non-uniform water distribution which was caused primarily by incomplete forming of the grooves in the oxygen side flow field of the current collectors. Pre-forming of the titanium foil prior to collector molding has made a significant improvement in the uniformity of the flow field and has reduced the module flow impedance by approximately 40%. A 20 cell, 1 ft^2 module containing these improved collectors is currently on test at 240°F with no indication of membrane attack after 150 hours of operation.

Reduced Cell Impedance

Significant performance improvements as a result of reduced membrane thickness and reduced collector impedance were demonstrated in GFY 81. These improvements are shown in Figure 1.

A six-cell module of 2.5 ft^2 cells (DOE 46) using 7 mil thick solid polymer electrolyte versus the standard 10 mil thick membrane demonstrated a 75 mV improvement due to reduced membrane resistance plus an approximate 35 mV improvement due to collector resistance decrease.

Subsequently, a 20 cell, 1 ft^2 module (NMPC #1) was assembled utilizing standard 10 mil membrane, but with collectors which had been fabricated using optimized material control procedures. This module demonstrated a 70 mV improvement due to reduced collector resistance. This unit is currently under test at 240°F.

As indicated in Figure 1, the combination of optimized collectors and reduced membrane thickness promises performance at 240°F in the 1.70 VDC range at 1000 ASF current density.

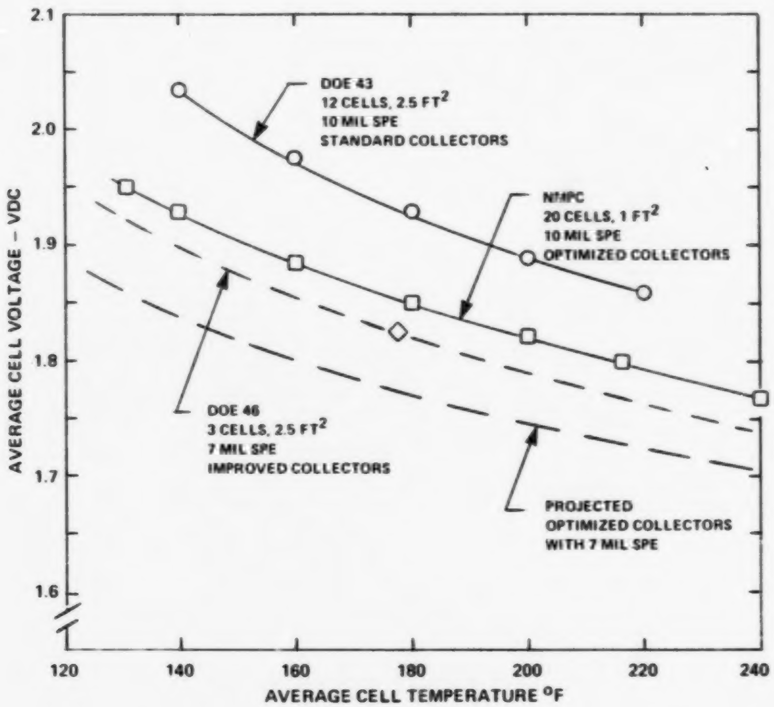

Figure 1. Cell Performance Vs. Temperature - 1000 ASF

Long-Term Life Testing

Under ESEERCO sponsorship, endurance testing of 1/20 ft^2 laboratory sized cells has continued throughout the past year. Highlights of this testing are:

- More than 33,000 hours have been achieved to date on a carbon collector cell at 180°F.
- More than 14,000 hours have been accumulated to date on a 4 cell stack of present technology (fluoropolymer/carbon collectors and advanced WE3 oxygen side catalyst) cells at 180°F.
- More than 2,800 hours were achieved on a present technology cell at 240°F.

Techno-Economic Study

As part of the GFY 81 DOE program, a techno-economic study is in progress to a) quantify the cost of hydrogen produced by SPE water electrolyzers as a function of design and operational parameters, b) establish the sensitivity of the hydrogen cost to the various parameters; and c) define the operating conditions for the optimum cost of hydrogen. As part of this study, projected cost information for a 2 MW system has been supplied to Arthur D. Little for a comparative analysis which is being performed by ADL under contract to DOE.

500 SCFH Prototype System

Figure 2 is a photograph of the prototype Model ES-1000 Electrolysis System developed under EPRI and PSE&G sponsorship. The system is designed to accommodate electrolysis modules of 100 to 500 SCFH capacity. The prototype system utilizes a 200 SCFH module containing fourteen 1 ft^2 cells. The module is shown in Figure 3. The system has currently completed four weeks of a scheduled 12 week in-house test sequence prior to being installed in the PSE&G Sewaren, New Jersey facility for two years of field testing. Figure 4 shows the module performance to date. The system is designed to operate at 100 psi hydrogen delivery pressure at a current density of 1000 ASF and a 130-140°F module operating temperature range.

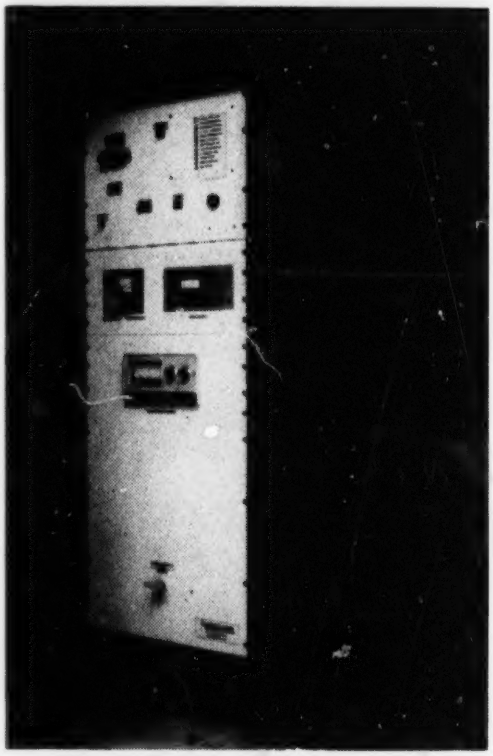

Figure 2. 500 SCFH SPE Electrolysis System

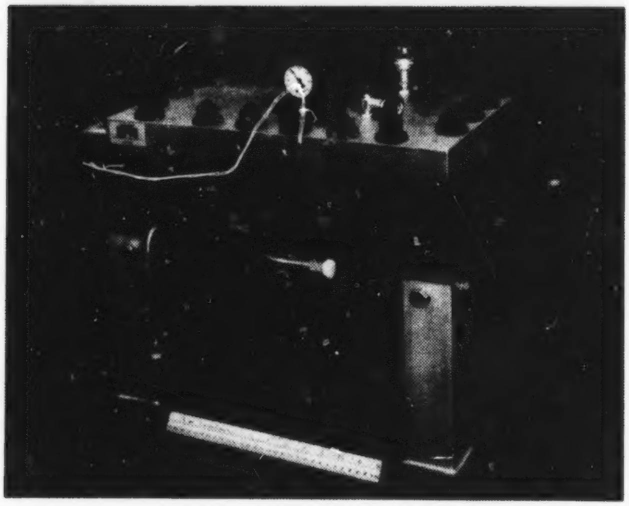

Figure 3. 200 SCFH (1 Ft^2) Water Electrolyzer

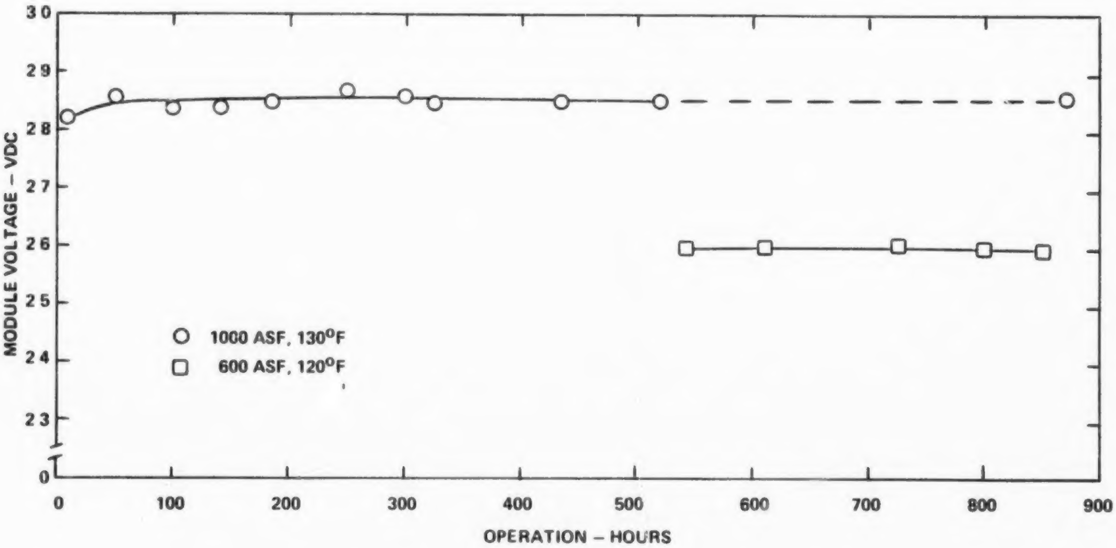

Figure 4. Performance Vs. Time - EPRI/PSE&G 200 SCFH Module - 14 1 Ft^2 Cells

PROJECT SUMMARY

Project Title: Advanced Alkaline Water Electrolysis; Development of Electrolysis Cell Separator for 125 C Operation

Principal Investigator: John N. Murray

Organization: Teledyne Energy Systems
110 West Timonium Road
Timonium, Maryland 21093

Project Goals: (Current) To demonstrate polybenzimidazole (PBI) and/or potassium titanate (K_2TiO_3) separators are useful for alkaline solution, water electrolysis at temperatures to 125 C. (Overall) The project is directed to identification of improved electrochemical cell components which exhibit stability at operating temperatures of 100 to 150 C, operating current densities of approximately 500 ma/cm^2 and attain an overall process efficiency approaching 100%.

Project Status: The current contract is directed to the development and testing of an improved electrode separator for sustained operation above 100 C. The use of porous PBI and admixed PBI/K_2TiO_3 as a porous separator is being investigated, both compounds having previously been shown to have chemical stability in hot alkaline solutions. The apparently mechanically stable high density, porous all PBI separators have been found to influence the internal cell resistance by an additional 80% relative to the equivalent asbestos separator. The investigation of the PBI/K_2TiO_3 separators has just been initiated and is hoped to allow the same mechanical stability at lower overall densities.

The summary report for Contract BNL 507416-S was submitted to BNL in May 1981. The effort concentrated on testing improved electrodes and separators using both TES supplied minicells (50 cm^2) and the applied research size (300 cm^2) five-cell modules in ARIES, the test system developed under a previous BNL contract. The advanced cathode, the C-AN electrocatalyst coating on a nickel wire screen substrate developed by the British Petroleum Research Centre, was tested with conventional and potentially improved anodes and electrode separators. A slight improvement in the initial performance of higher surface area, porous nickel anodes (~50 mV at 500 ma/cm^2) was demonstrated and the higher surface area nickel anodes appear to have quite stable voltage-time characteristics when operated under constant current conditions. Two alternative anode electrocatalysts tested in the 50 cm^2 cells showed moderate improvements (100 to 150 mV) although development work is required prior to use of these compositions in ARIES or commercial systems. Separator development was limited to the use of asbestos and the electrochemical improvement of 125 mV (373 ma/cm^2, minicell test fixture) was demonstrated by decreasing the separator thickness from 0.046 to 0.020 cm. Little electrochemical differences were observed in varying the asbestos density between 40 and 90% in this thickness range. The gas transmission, break through pressure for the wetted separator was decreased from a normal value of >80 psid to values of 10 to 60 psid for the 0.020 and 0.025 cm thick pieces which should still be adequate for commercial, dual irriguous electrolysis cell designs. The associated problems in attempts to utilize these thinner separators within an existing module design (e.g., ARIES) was identified and is associated more with the cell frame and edge sealing designs for both the separator and bipolar plates. Based on the data from the minicell and ARIES testing program, an overall process efficiency (AC into H_2 output) of 80% is projected with module voltage efficiencies projected to be 91% for optimal 100 C technology and 97% for optimal 125 C technology.

Contract Number:	BNL 545767-S	BNL 507416-S
Contract Period:	1 April 1981 - 30 September 1981	1 February 1980 - 30 April 1981
Funding Level:	$115,840	$154,542
Funding Source:	Brookhaven National Laboratory/U. S. Department of Energy	

ADVANCED ALKALINE WATER ELECTROLYSIS

John N. Murray
Teledyne Energy Systems
110 West Timonium Road
Timonium, Maryland 21093

ABSTRACT

The testing of five-cell, 300 cm^2 active area, alkaline electrolyte, electrolysis modules for hydrogen production was continued as part of BNL 507416-S with the emphasis placed on demonstrating improvements via the anode (O_2 evolution electrode) and the interelectrode separator. The cell voltage can be improved by 50 to 75 mV/cell (500 ma/cm^2, 100 C) by use of a higher surface area, pure nickel anode structure which also appears to offer greater voltage-time stability. Alternative electrocatalysts tested in 50 cm^2 minicells exhibited up to 150 mV/cell improvement at relatively low current densities. Further electrode development is required to increase the macroporosity and minimize voltage restricting diffusional processes. Testing porous asbestos separators of varying thickness and density in both 50 and 300 cm^2 cells showed the possibility of improving the cell voltage 125 mV by reducing the thickness from the centerline 0.046 cm to 0.020 cm. Therefore, proper electrode selection can lead to module voltage efficiencies of 85% at moderate (75 C) operating temperatures. A new six-month contract effort, BNL 545767-S was initiated in April 1981 to develop and test porous polybenzimidazole (PBI) and admixed PBI/potassium titanate (K_2TiO_3) separators. Tests of both components have previously indicated chemical stability in 125 C alkaline electrolyte environments. Preliminary test data indicate the use of high density, mechanically stable, pure PBI separators result in approximately 80% higher cell internal resistance values relative to the conventional asbestos separators. Fabrication and characterization of lower density, porous PBI pieces will proceed at a later date. Testing of the compression characteristics of these new separators and electrochemical testing of the mixed PBI/K_2TiO_3 separators has just been initiated at the time of preparation of this report.

INTRODUCTION

This report continues from last year's summary report /1/ and briefly summarizes the work at TES during GFY-81 on improving the state of the art of alkaline water electrolysis under two contracts to BNL, BNL 507416-S and BNL 545767-S. Technical supervision and guidance at BNL was again provided by Mr. A. Mezzina, Dr. S. Srinivasan, and Mr. M. F. Bonner whereas supervision at the U. S. Department of Energy (DOE) was provided by Drs. F. Gornick and R. Reeves. At last year's meeting, the 1500-hour test of the improved cathode technology was reported. Dubbed the C-AN cathode electrocatalyst, the material developed by the British Petroleum Research Centre /2/ required input levels of 1.73 volts/cell at 500 ma/cm^2, 100 C. The testing involved the use of the TES-supplied 300 cm^2, five-cell test module and the Applied Research Industrial Electrolysis System (ARIES) developed in 1978 under a previous contract. A series of subsequent new module tests were planned. Based on successful preliminary results using PBI as an interelectrode separator, further testing of this material was planned as part of BNL 507416-S. During this time period, Celanese, fabricator of PBI, was involved in a corporate decision with regard to establishing PBI as a significant business venture. This decision was made in late 1980 /3/; a small quantity of PBI fibrids was made available and the testing of this PBI is one of the key tasks of Contract BNL 545767-S. In addition to testing improved separators, testing of improved anodes was planned and at the time of last year's report, the anode screening module (No. 14) had been constructed for testing. Several approaches to an improved anode were of interest including two approaches to a higher surface area nickel electrocatalyst, the possible improvements via the perovskite structures and a new proprietary anode electrocatalyst dubbed the A-380 anode.

The BNL 507416-S contracted effort was completed on 30 April 1981 and the summary report was submitted to BNL as TES-507416S-16 in May 1981. The first section of this summary reiterates the summary from that report. Following several discussions with BNL personnel, work on a six-month, follow-on contract was initiated which is concentrating on establishing several key properties of PBI and PBI/K_2TiO_3 electrode separators. Some of the relevant test data obtained to date are included in this second discussion section.

CONTRACT BNL 507416-S SUMMARY

The three primary tasks involved in Contract 507416-S were (a) the electrolysis component development and testing in ARIES; (b) a review and analysis of the available corrosion literature with regard to the projected usefulness of the various metals in the 125 C electrolysis environment; and (c) participation in the International Energy Agency (IEA), H_2 R&D program as requested by BNL. As noted in the introduction, the primary technical emphasis with respect to the components testing was with regard to new, high temperature cell separators and new improved anodes.

When PBI became unavailable, it was agreed that demonstration of the merits of thinner separators could be accomplished by preparation of various density asbestos pieces although previous test results have indicated that use of the asbestos separators above 100 C would be quite limited with respect to operating life.

Corresponding TES-funded studies using the 50 cm^2 minicell hardware showed 0.125 volt improvement could be realized (373 ma/cm^2) when the separator thickness was lowered from 0.046 to 0.020 cm. Little electrochemical differences were observed in varying the asbestos density between 40 and 90% in this thickness range. The gas transmission, break through pressure for the wetted separator was decreased from a normal value of >80 psid to values of 10 to 60 psid for the 0.020 and 0.025 cm thick pieces which should still be adequate for commercial, dual irriguous electrolysis cell designs. ARIES test modules No. 15 and No. 18 were constructed with conventional HS screen electrodes and the separators compressed to 52 and 61% density at 0.025 cm thickness. The general improvement observed at 100 C, 500 ma/cm^2 was a voltage savings of approximately 5% (~0.10 volt). The thin asbestos separators were also tested using the C-AN cathodes in module No. 18 and an attempt was made to utilize the thin separators with the C-AN cathodes and higher surface area anodes (module No. 19A). The initial performance of module No. 16 was good--1.73 V/cell, 500 ma/cm^2, 100 C and, as usually observed, the cells improved by between 100 and 130 mV within the first 150 hours of testing. The test was discontinued at approximately 440 hours because of questionable voltage data possibly being the result of a module internal gas product cross leak. All of the 300 cm^2 modules prepared with 0.025 cm thick separators exhibited a small initial cross leakage of about 5 to 20 sccm at 5 psid, beyond the specification limit of <1 sccm at 5 psid. In that the module was expected to operate with a very low (<1 psid) differential pressure, no problems were anticipated. The cause of the cross leakage appears to be the result of attempting to utilize the thin separators in a cell frame designed for a 0.075 cm thick separator and the lack of sufficient stress on this wet seal and the equivalent adjacent bipolar seal. The simple redesign of the cell frames would, however, involve changing the injection molding tools, an expense beyond the limits of this contract.

Two types of K_2TiO_3 electrode separators were also made available for testing using the minicell hardware. One type was the K_2TiO_3 impregnated porous Teflon (PTFE) /4/ supplied to TES by the Government Industrial Research Institute (GIRI) of Osaka, Japan through TES/BNL participation in the International Energy Agency (IEA) Annex IV on the R&D into hydrogen production. Two thicknesses of separators (0.04 and 0.07 cm) were tested and found to allow gas transmission through the KOH-wetted separators indicating a 20-micron pore structure. The TES cell designs require a maximum pore size of 3.5 microns; the test information was summarized and submitted to GIRI personnel with the hope of obtaining the smaller pore diameter samples in CY '81. The second type of porous titanate separator using a PTFE binder also exhibited significant cross leakage at 2 psid. The manufacturer suggested the submitted samples were intended for alkaline battery applications and therefore had a pore diameter range of 20 to 40 microns. Attempts will be made to obtain samples with pores in the <3.5 micron range for safe testing and usage in electrolysis cells of the TES design.

Basically, two distinct approaches to improvements via the anode were attempted. The long-term stability of the nickel/nickel oxide anode electrocatalyst in alkaline electrolytes leads to attempts to lower the polarization losses by increasing the effective surface area of the anode. Samples prepared by the MPD Technology Corporation; thermally sintered, porous, carbonyl nickel powder electrodes and the conventional TES-HS nickel screen anodes allowed a reasonably wide approximate surface roughness range from 5 to 250 for evaluation. Assuming an anodic Tafel slope of 75 mV/decade current density, one would anticipate an improvement of 127 mV if an equivalent quantity of surface were active for each test piece. Both minicell and ARIES module test results (modules No. 14, 17, and 19) showed some of the anticipated (50 mV) gain was realized. In module No. 19 endurance testing, the higher surface area anode did not exhibit the normal voltage loss-time pattern observed with the conventional anode cells when operated under constant current density conditions. This is the first observation of a stable cell voltage during the period of about 1.5 to 170 hours of continuous operation. Normally, a loss of 40 to 60 mV/decade time (80 to 120 mV loss for this reported interval) would be observed. Further testing is warranted when the separator selection has been made.

Alternatives to the "pure" nickel anode catalyst have been suggested in the literature for several years. Previous testing at TES showed no particular advantage to the use of Co_2NiO_4 at a 10 mg/cm^2 catalyst loading whereas at 40 mg/cm^2, a slight voltage improvement was observed. Two new catalyst systems were investigated during the contract period. A preliminary evaluation of the $NiLa_2O_4$ and $Co_{0.2}Ni_{0.8}LaO_3$ perovskite catalyst coatings on the conventional HS nickel wire screen showed one catalyst preparation to be particularly effective, the $NiLa_2O_4$. These initial (4 to 6 test hours) electrochemical characteristics of the samples prepared by Professor G. Fiori (University of Milan) were quite similar to the results Dr. Fiori has disclosed /5/ although the use of these oxide coated electrodes may cause some contact resistance problems when using the electrodes in practical cell assemblies. The voltage savings using the $NiLa_2O_4$ sample ranged from 70 to 100 mV (30 to 500 ma/cm^2, 57 C, single irriguous minicell tests) and a further look at this catalyst system is warranted. A second, proprietary anode catalyst system, coded A-380, was evaluated using both minicell and ARIES hardware. The reported research (1 to 2 cm^2 samples) results suggested a significant improvement--100 to 150 mV, 500 ma/cm^2, 70 C. ARIES testing did not confirm these data, the voltage data at 500 ma/cm^2, 100 C during the 595-hour testing of module No. 14 being 100 to 150 mV inferior to the conventional HS nickel screen anode being tested in the same module. Subsequent evaluation in the minicell hardware showed the catalyst to be effective in the 10 to 100 ma/cm^2 range where a 120 to 160 mV improvement was observed. Examination of the test electrodes indicates the observed high voltages at the higher current densities and in the ARIES test may be associated with too-heavy a catalyst coating on the support screen. In the TES cell design, this would lower the required transport processes through the electrode macropores leading to excessive concentration polarization. Further A-380 catalyst/electrode development work has been initiated.

The second task involved a survey of the relevant literature to establish which metals would be applicable for the advanced electrolysis systems at temperatures up to 150 C. The summary report which was submitted to BNL concluded that for operation in the 110 C to 150 C range, nickel 200, nickel 201, Monel 400 and Inconel 600 appear to be required for the KOH (hot) wetted sections of the system. The use of AISI 310 and 316 stainless steels has economic advantages but there is insufficient data to justify the use of these materials for hydrogen plants expected to operate for beyond 20 years. For the operating range of 80 to 110 C, types 304 and 316 stainless steel appear to be applicable with the same general caveat. Test loop evaluation of these metals is required to demonstrate negligible problems are observed in a 10,000-hour (minimum) test.

Therefore, at the end of the contract period, all the pieces for an 80% efficient hydrogen production process have been identified and several of the components have been tested in the minicell (50 cm^2) or ARIES (300 cm^2) units. With respect to the module designed for operation at 500 ma/cm^2, the use of the C-AN cathode with a thin stable separator or an improved anode would allow 1.63 volts/cell at 100 C or 1.53 volts/cell at 125 C, corresponding to voltage efficiencies of 91 or 97% respectively. A key element requiring improvement is the separator which will remain mechanically stable and allow operation at the 125 C range. This is the subject of the follow-on effort.

CONTRACT BNL 545767-S SUMMARY

This six-month effort is aimed mainly at identifying the required characteristics of a chemically and mechanically stable electrode separator. The two approaches being considered from the development viewpoint are the use of PBI fibrids in a moderately high density range (50 to 80%) or the use of an admixed PBI/K_2TiO_3 separator. Part of the initial testing involved preparation of asbestos separators to clarify and demonstrate some of the TES-funded findings reported in the BNL 507416-S summary report. The three primary characteristics of the separators that are of immediate interest are (a) the adequate mechanical strength and stability; (b) the formation of reasonably small pore sizes to preclude gas transmission through the electrolyte-wetted pores at moderate differential pressures (Δp); and (c) sufficient porosity (through pores) to minimize the ionic current, voltage losses which constitute the largest portion of the bipolar plate style cell, internal resistance voltage loss.

At the time of this report, most of the characteristics of the pure PBI separator have been evaluated and only preliminary data on the admixed PBI/K_2TiO_3 separators have been obtained. The compressive stress/strain and compressive creep determinations are scheduled to be evaluated during the last two months of the contract.

The minicell internal resistance values as determined via regression analysis of the corresponding V-A data sets suggest the equivalent pure PBI separator will cause about 80% more ionic resistance than the asbestos piece. Gas transmission for pieces 0.05 cm and thicker with apparent densities of greater than 50% were found to be negligible for Δp values up to 80 psid. Pieces 0.038 to 0.045 cm thick retained gas Δp levels up to the 10 to 20 psid range, probably satisfactory for commercial usage although a material maldistribution could account for the lower observed Δp values.

The work with the mixed PBI/K_2TiO_3 samples had been initiated just prior to the start of preparing this summary report. There are two general approaches to the mixed material separator. One utilizes a small quantity of K_2TiO_3 as a spacing agent within the main PBI matrix and therefore should eliminate or retard the compressive creep of the porous organic portion of the separator. The alternative approach is the preparation of a K_2TiO_3 separator using a small quantity of PBI as a binder. Although Teflon bonded K_2TiO_3 separators have been used in fuel cells for over 10 years, the advantage of using PBI as the binder would be in the formation of a totally wettable and mechanically stronger piece. The first samples tested have been of the K_2TiO_3 spacer type and the initial results are showing these samples to be stiffer than pure porous PBI but give equivalent electrochemical characteristics.

The mechanical testing which remains will involve determining the compression characteristics of all three types of separators at ambient and 125 C. The mechanical stability is important from two aspects in the TES cell designs. The TES design approach relies on a predetermined, preset strain being maintained to assist in minimizing electrical contact problems associated with the electrode/bipolar plate assemblies. Additionally, the through porosity of the separator affects the electrolyte conductivity and therefore should not decrease significantly with operating time. When a mechanically and electrochemically satisfactory separator is identified, the next obvious step will involve preparation and endurance testing in the larger ARIES type hardware.

CONCLUSIONS

The electrocatalysts/electrodes and general operating conditions for a high efficiency d.c. electrolysis system for the production of hydrogen have been identified. The stable C-AN cathode catalyst coupled with the A-380 anode catalyst or a high surface area (e.g., a porous nickel battery plaque) anode should result in a cell operating at 1.65 V/cell, 500 ma/cm^2, 100 C and a projected 1.55 V/cell at 125 C. Demonstration of a satisfactory and mechanically stable porous electrode separator remains. In the event only asbestos separators have satisfactory characteristics, cell operation would be limited to approximately 80 C for long-life operation and the resulting cell voltage would appear to be approximately 1.725 at 500 ma/cm^2. Although some electrode fabrication development work still remains, the next steps should include (a) construction and testing of a moderate sized (~50 KW) system based on at least the advanced electrode technology; (b) construction and testing of plumbing test loops to evaluate the corrosion and/or usefulness of type 310 and 316 stainless steels as well as electrolyte pumps at 125 C; (c) continued life testing of the advanced electrode and separator pieces; and (d) cell scale-up design studies should be initiated to establish inexpensive, large-area cells for the near-future moderate sized renewable resource applications and demonstrations.

ACKNOWLEDGMENTS

Module testing in ARIES and the minicell testing during BNL 507416-S was performed by C. W. Heusler under the supervision of V. R. Lougheed. The minicell evaluation and separator preparation under BNL 545767-S is again by C. W. Heusler. Mr. J. W. McGrew was responsible for the corrosion literature survey and final report under BNL 507416-S. The author again thanks Ms. M. F. Gembarosky for upgrading the level of the program reports and L. W. Mickle for the preparation of the program artwork.

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PROJECT SUMMARY

Project Title: Static Feed Water Electrolysis for Large Scale Hydrogen Generation

Principle Investigator: F. H. Schubert

Organization

Life Systems, Inc.
24755 Highpoint Road
Cleveland, OH 44122
(216) 464-3291

Project Goals:

Demonstrate the inherent capability of the alkaline electrolyte, Static Feed Water Electronlysis System (SFWES) to generate low cost hydrogen for chemical storage/industrial chemical applications.

Reductions in capital and operating costs will be addressed through cell area scale-up demonstrations (1.0 ft^2) and studies (5 ft^2); operation at high current density (1,000 ASF); demonstration of low cell voltage operation; and testing with contaminated feed water, e.g., simulated sea water, to eliminate water treatment expendables and equipment.

Project Status:

The project is approximately 90% completed. The elevated current density testing and the testing with contaminated water have been successfully completed. At 1,000 ASF and 180 F the static feed cell with super electrodes maintained a steady-state voltage of 1.81 volts. Cells being operated with plain tap water and with simulated sea water have been tested for over 1,700 hours and 1,100 hours, respectively, without signs of performance degradation.

Scale-up studies are being completed. Life Systems has fabricated a 1.0 ft^2 single cell for testing and is completing its scale-up analysis for large scale hydrogen production.

An extension to the current contract is anticipated to allow for testing of the 1.0 ft^2 cell hardware. The Final Report will be submitted following the 1.0 ft^2 tests.

Contract Number: BNL-522723-S

Contract Period: August 15, 1980 - August 31, 1981

Funding Level: $114,409

Funding Source: U.S. Department of Energy through Brookhaven National Laboratory

STATIC FEED WATER ELECTROLYSIS FOR LARGE SCALE HYDROGEN GENERATION

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ABSTRACT

The static feed water electrolysis concept, developed by Life Systems, Inc., is being evaluated for application to large-scale hydrogen generation. The inherent potential for low cost and high performance of this alkaline electrolyte-based technique resulted in the award of a twelve-Month, Department of Energy funded program to Life Systems, Inc. The effort addresses four areas: (1) definition of upper current density levels possible with the static feed concept, (2) investigation of operation with contaminated water sources (e.g., seawater), (3) scale-up of cell area, and (4) definition of future scale up at the cell stack and system level.

This paper presents the static feed concept and results to date of each of the four program tasks.

INTRODUCTION

Over the past ten years, Life Systems, Inc. has developed a unique water electrolysis technology that offers the potential of significantly reducing the cost of bulk hydrogen generation through water electrolysis. Specifically, these cost reductions result from:

1. A simple, capital equipment-saving technique for feeding the water into the water electrolysis cell.
2. The development of an oxygen evolving electrode that has demonstrated superior performance (1.49 V at 150 ASF and 180 F after 18,000 hours).
3. The use of an alkaline electrolyte, which is compatible with low cost materials.

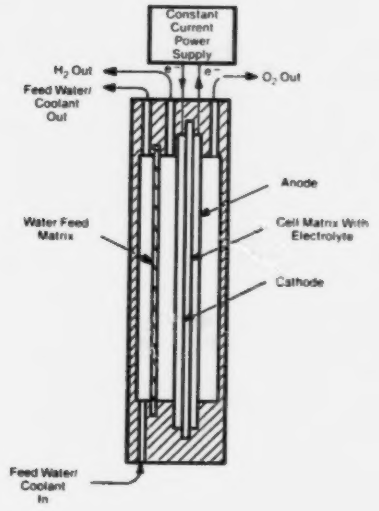
This technology, however, has been limited to smaller electrode areas (0.1 to 0.3 ft^2) and to modules of up to 15 cells. Thus, although the technology is extremely attractive, the state of its development requires scale-up in several key areas to realize the performance and cost reduction expectations.

To achieve these goals, Brookhaven National Laboratory (BNL), under sponsorship of the Department of Energy (DOE), has initiated a development program with Life Systems, Inc. to demonstrate the capability of the static feed water electrolysis system to satisfy the bulk hydrogen generation requirements of the BNL/DOE Chemical/Hydrogen Energy Systems Program.

ALKALINE ELECTROLYTE, STATIC FEED WATER ELECTROLYSIS CONCEPT

The half cell and overall electrochemical reactions for the static feed cell using an alkaline electrolyte are shown in Figure 1 together with a functional schematic of a static feed cell.

The static water feed concept operates as follows. Water diffuses in its vapor state across the hydrogen cavity into the cell matrix where it is electrolyzed. The driving force for vapor transport is a concentration difference between the water source in the feed compartment of the cell and the aqueous electrolyte retained by capillary fources in the cell matrix. No liquid feed water contacts the electrodes. More detailed description of this concept and its operation are presented elsewhere.



REACTIONS	
CATHODE	$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$
ANODE	$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$
OVERALL	$2H_2O \longrightarrow 2H_2 + O_2$

FIGURE 1 STATIC FEED WATER ELECTROLYSIS FUNCTIONAL CELL SCHEMATIC AND REACTIONS

TECHNOLOGY DEVELOPMENT PROGRAM

The four task development program is currently being completed. The scope of the proposed total effort was to:

1. Define the upper current densities possible with the static feed concept.
2. Define the ability of the static feed water electrolysis concept to operate with contaminated water.
3. Demonstrate hardware scale-up of the electrode area from the present 0.1 ft^2 to 1.0 ft^2 or larger.
4. Establish a sequence to follow in future scale-ups of static feed hardware (of electrode area, bi-polar plates, number of cells per module, etc.) that will result in larger gas generating capacity.

Elevated Current Density Investigation - Task 1

The capital cost of water electrolyzers stacks is directly proportional to the number of electrolysis cells. Hence, capital cost is inversely proportional to operating current density. A series of experiments were completed to investigate and demonstrate performance at elevated current density (1,000 ASF or greater).

Baseline configuration cell hardware, having an active area of 0.1 ft^2, was used to characterize cell performance as a function of current density and to determine if any limit in water vapor transport would be encountered up to the Task 1.0 goal of 1000 ASF. Two anodes, one an intermediate (WAB-1) the other a high performance (WAB-6) type, were tested. The results for 180 F operation are shown in Figure 2. No limits in water vapor transport were observed.

To determine the contribution of the individual electrodes (i.e., anode and cathode) to the overall cell voltage and to observe possible performance limits at either electrode, half cell voltages versus the Standard Hydrogen Electrode (SHE) were also measured. This data is shown in Figure 3. Again, no limits with respect to current density for the levels investigated were observed.

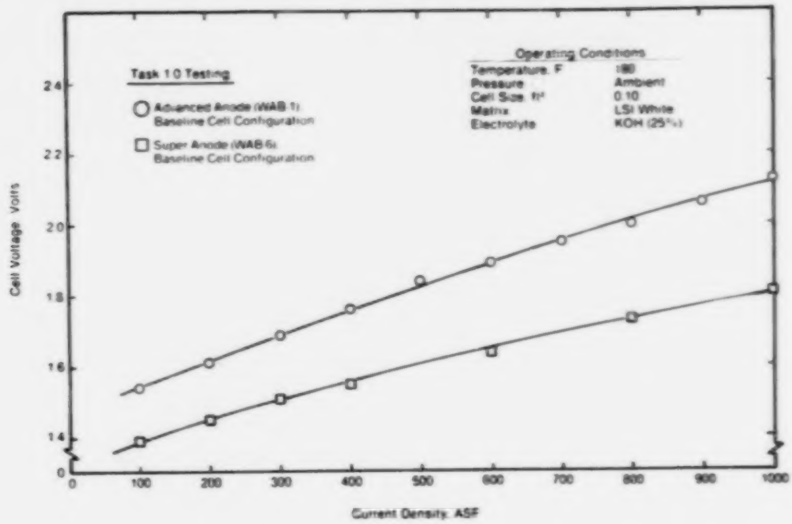


FIGURE 2 CELL VOLTAGE VERSUS CURRENT DENSITY

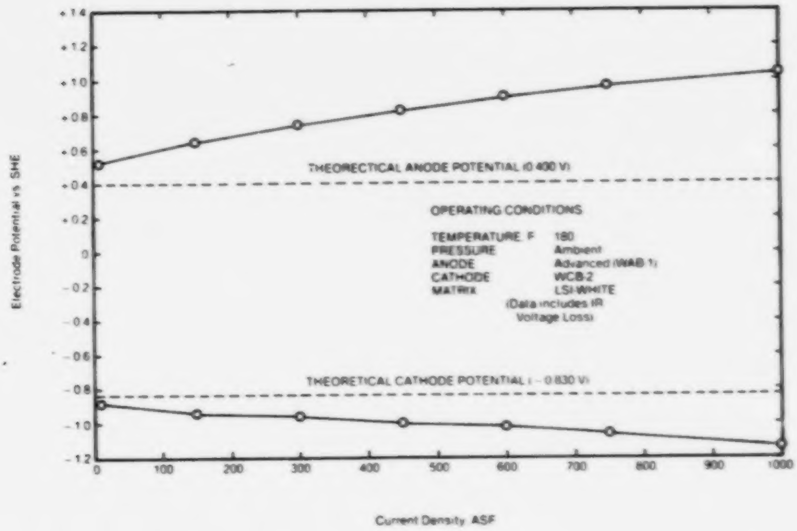


FIGURE 3 HALF CELL POTENTIALS VERSUS CURRENT DENSITY

Contaminated Water Operation - Task 2

A significant part of the present cost of bulk hydrogen generation through water electrolysis is incurred during the purification of the water to be electrolyzed. Purification is necessary to prevent contamination of the electrode catalyst and/or cell electrolyte. In the static feed system, however, the liquid water to be electrolyzed is separated from the electrodes and cell electrolyte by a gas compartment containing only water vapor and hydrogen.

As a first step to eliminate water purification, Life Systems had already demonstrated the ability of its static feed water electrolysis system to operate using deionized feed water (as opposed to an aqueous solution of potassium hydroxide) in the water feed compartment. The next step, demonstrated under this task, was to replace the deionized water in the water feed compartment with tap water, brackish water and/or simulated seawater.

Two cells were tested. One of the cells used a simulated sea water mix (used for salt water aquariums) as its water source, the other cell used untreated city tap water. The performance of these two cells was very nearly equal to the performance observed in baseline cells at similar operating conditions. A total of 1720 hours of operation were accumulated with the tap water cell and 1150 hours with the sea water cell. Performance levels versus time for the two cells are shown in Figures 4 and 5. Testing was halted to inspect the cells. No anomalities were observed with the tap water cell. The cell using simulated sea water showed some small amount of corrosion on the nickel anode current collector and anode. The corrosion may have been caused by an accidental flooding (with salt water) of the cell 80 hours into the test. More testing has been recommended in this area.

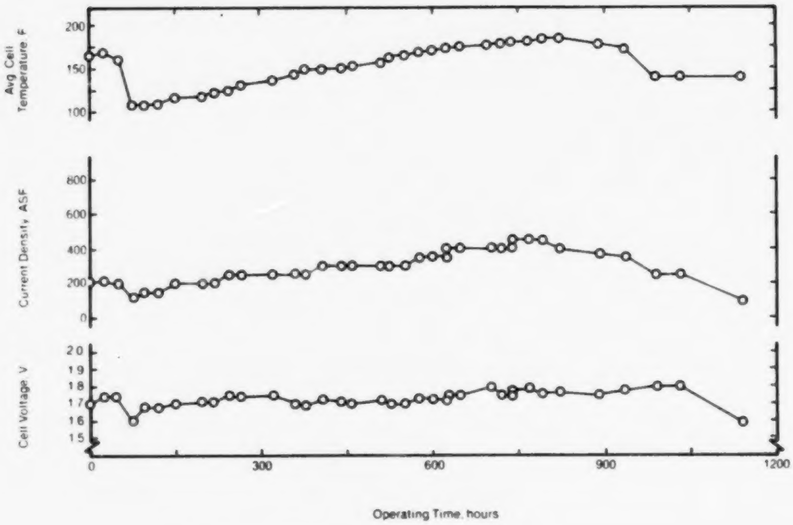


FIGURE 4 CELL PERFORMANCE VERSUS TIME USING SIMULATED SEA WATER FEED

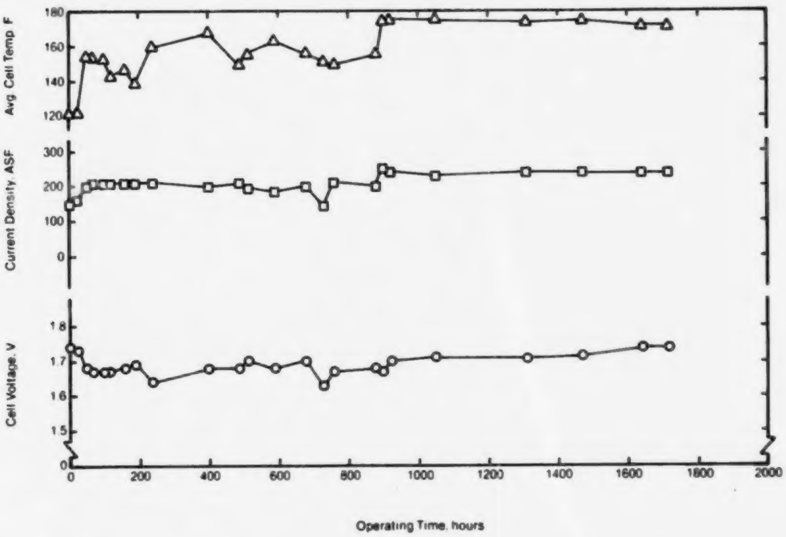


FIGURE 5 CELL PERFORMANCE VERSUS TIME USING TAP WATER FEED

Cell Area Scale-Up - Task 3

The larger the electrolyzer cell area, the fewer number of cells that are required to generate a given volume of hydrogen. Reduction in the number of cells through increasing the active cell area reduces capital cost and keeps the number of cells within practical limits for large-scale gas production.

Sizing calculations for the SFWES style concept have been completed for 1.0, 5.0 and 10 ft^2 cells. In parallel Life Systems is developing actual scaled-up cell hardware having an active area ten times the present baseline size, or 1.0 ft^2. Major characteristics of the 1.0 ft^2 cell are:

- Active Cell Area: 1.0 ft^2
- Electrode Types WAB-1 and WCB-2 (Advanced)
- Nominal Current Density: 400-800 ASF
- Operating Temperature: 200 F (Max)
- Operating Pressure: 550 psig (Max)

All design and fabrication work of the 1.0 ft^2 cell and of the manufacturing facilities has been completed. Based on trial assemblies, some minor modifications have been identified and are being implemented.

Future Scale-Up Sequence - Task 4

Studies completed at BNL and elsewhere have indicated that end-item applications of water electrolyzers for bulk hydrogen generation require electrodes of 2 to 12 ft^2 in area.

BEST DOCUMENT AVAILABLE

In this task the future scale-up sequence to be followed for the static feed water electrolysis concept is being established. The goal has been low development risk and minimum development cost. Some of the factors that are being considered are:

1. Electrolyzer Stack Related
   - The ability to fabricate electrodes of larger sizes (e.g., up to 10 ft^2).
   - The ability to prepare matrices of a size similar to that of the electrodes.
   - The ability to stack a large number of cells in series.
   - The ability to construct low resistance, low cost bi-polar current collectors.
2. System Level Related
   - The ability to scale-up the peripheral system components.
   - The ability to simplify the system
     - Component elimination
     - Low water quality
     - Low parasitic power

Table 1 summarizes the manufacturing capabilities and requirements for electrolyzer cell sizes of 0.1, 1.0, 5.0 and 10.0 ft^2. Present capabilities and future implementation are indicated in Table 1.

A key characteristic is the simplicity of the static feed-based electrolysis system, as demonstrated in Figure 6. Elimination of components reduces scale-up needs and development funds. A potential scale-up development sequence has been prepared and is shown in Figure 7.

TABLE 1 ELECTROLYZER MANUFACTURING CAPABILITIES/REQUIREMENTS

	Cell Size, $ft.^2$				Comments
	0.1	1.0	5.0	10.0	
Electrodes	x[a]	x	Added manufacturing facilities		All manufactured at LSI
Matrices	x	x	Added manufacturing facilities		Added large fixture for 5 and 10 ft^2 matrices
Current Collector	x	Fixtures needed Collectors in Multicell Modules[b]			Outside Vendor
Insulation Plates	x	x	x	x	Outside Vendor
Endplates	x	x	x	x	Outside Vendor
O-rings	x	x	x	x	Outside Vendor
Support Screens	x	x	x	x	Manufactured at LSI, no additional capability needed
Cell Frame	x	3 Molds for Cell Frame (one for each cell size)[c]			Outside Vendor

(a) X = Capability aready resists.
(b) Three welding fixtures needed for 1.0, 5.0, and 10 ft^2
(c) Molds will be used toward the end of the development phase. Early development work will use machined parts.

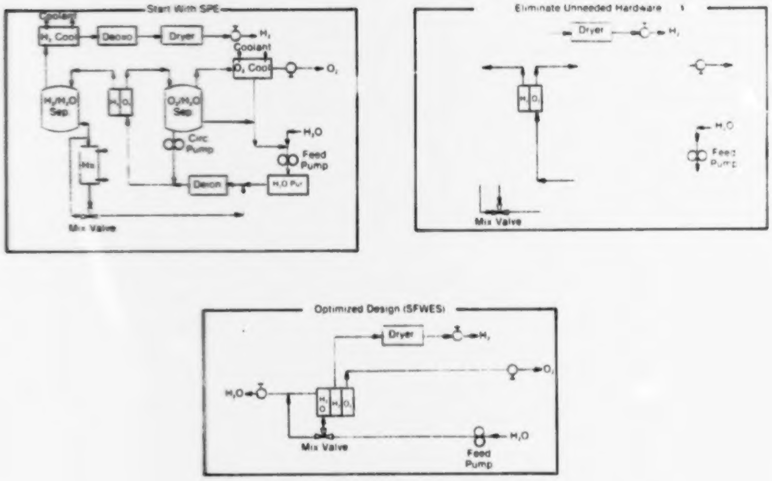

Start With SPE
Coolant
H₂ Cool
Deoxo
Dryer
H₂
Coolant
O₂ Cool
O₂
H₂/H₂O Sep
H₂ O₂
O₂/H₂O Sep
Circ Pump
H₂O
Feed Pump
Hx
Deion
H₂O Pur
Mix Valve
Eliminate Unneeded Hardware
Dryer
H₂
H₂ O₂
H₂O
Feed Pump
Mix Valve
Optimized Design (SFWES)
Dryer
H₂
O₂
H₂O
H₂O H₂ O₂
Mix Valve
Feed Pump
H₂O

FIGURE 6 LARGE SCALE H_2 GENERATION PLANT - SCHEMATIC COMPARISON OF CONCEPTUAL DESIGN

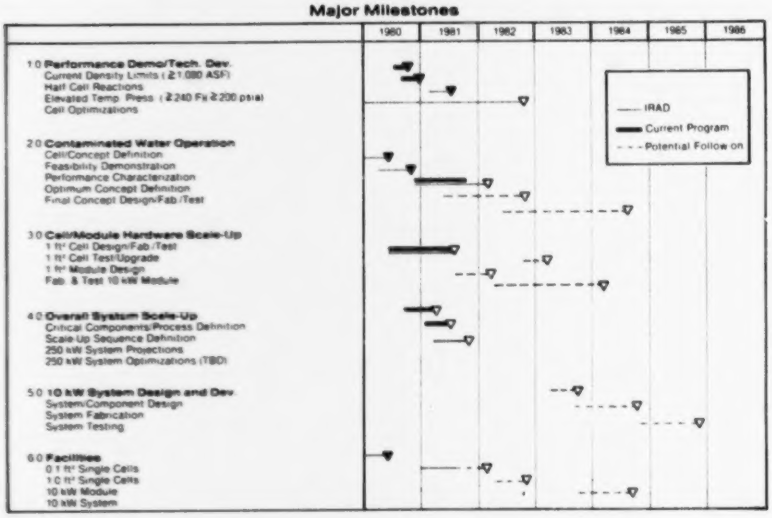


FIGURE 7 DEVELOPMENT SCHEDULE FOR STATIC FEED WATER ELECTROLYSIS FOR LARGE SCALE HYDROGEN GENERATION

SUMMARY AND CONCLUSIONS

The static feed electrolysis concept using an alkaline electrolyte is a viable candidate for large-scale, low cost hydrogen production. Its demonstrated performance surpasses that of other existing systems. Its inherent system level simplicity, coupled with its use of low cost materials and tolerance to low level purity water, project low capital and operating costs. Scale-up must be evaluated to adopt the static feed concept to terrestial energy applications. The four task program sponsored by the Department of Energy has been a step in that direction.

PROJECT SUMMARY

Project Title:	Selection and Evaluation of Materials for Electrochemical Energy Conversion Devices: Electrochemical Evaluation of Nickel Whisker Electrodes
Principal Investigator:	G. E. Stoner
Organization:	Applied Electrochemistry Laboratory Materials Science Department University of Virginia Charlottesville, Virginia
Project Goals:	To determine the specific electrocatalytic properties of polycrystalline nickel whisker electrodes. To explain the voltage time behavior of nickel electrodes.
Project Status:	A method has been developed and refined to measure effective surface area of planar electrodes. The method yields reproduceable and consistent results. Highly accurate determinations of exchange current densities for hydrogen evolution on nickel plates and nickel whiskers indicate that there is no significant difference due to the unique microstructure of whiskers. Supportive evidence for reversible hydrogen absorption into nickel plate and nickel whiskers is obtained by monitoring changes in apparent capacitance during absorption and desorpton.
Contract Number:	BNL 5-22027-S
Contract Period:	August 1, 1980 through July 31,1982
Funding Level:	$72,000
Funding Source:	U. S. Department of Energy through Brookhaven National Laboratory

SELECTION AND EVALUATION OF MATERIALS FOR ELECTROCHEMICAL ENERGY CONVERSION DEVICES:
ELECTROCHEMICAL EVALUATION OF NICKEL WHISKER ELECTRODES

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and L. L. Scribner
Applied Electrochemistry Laboratory
Materials Science Department
University of Virginia
Charlottesville, Virginia

ABSTRACT

A method has been developed and refined to measure effective surface area of planar electrodes. The method yields reproducible and consistent results.

Highly accurate determinations of exchange current densities for hydrogen evolution on nickle plates and nickel whiskers indicate that there is no significant difference due to the unique microstructure of whiskers.

Supportive evidence for reversible hydrogen absorption into nickel plate and nickel whiskers is obtained by monitoring changes in apparent capacitance during absorption and desorption.

INTRODUCTION

This report is a presentation of research conducted under contract #522027-S at the University of Virginia during the past year. More specifically, the comparative evaluations of the electrocatalytic properties of conventional nickel 200 and nickel whisker electrodes for hydrogen evolution in alkaline solutions are reported. The techniques employed for this alkaline system may also be applicable to many other electrochemical systems.

Previous research performed at this laboratory indicates an improvement in the energy efficiency of the hydrogen evolution reaction for porous nickel whisker electrodes as compared to nickel 200 screens on an apparent area basis.(1) However, it was not determined whether the energy efficiency gained by the use of sintered nickel whisker electrodes was due to their extremely high surface area or due to some truly innate electrocatalytic property. The fundamental question of specific electrocatalytic behavior of nickel whisker electrodes, independent of their high surface area, is the principal objective of this research. As a result, standard quantitative comparative tests for electrocatalysis need to be developed and some basic questions concerning what determines an electrocatalyst are considered.

Scanning electron micrographs of nickel whisker electrodes in Figure 1 reveal their high porosity (∿ 85%) and their extremely high surface area to volume ratio. In addition, nickel whiskers have a unique metallurgical microstructure which could result in some interesting electrocatalytic properties. The grain size of these whiskers is typically 200 to 400 Å. Thus each whisker is composed of many small grains and has a large grain boundary area. There are relatively few other defects. Enhanced electrocatalysis could result from nucleation sites provided by the grain boundaries or possibly from the increased energy associated with these grain boundaries.

REPORT OF PRESENT WORK: NICKEL ELECTROCATALYSIS

Electrocatalytic behavior should be determined on a true surface area basis. Therefore, if a comparison of electrocatalytic ability on different electrodes is to be conducted, a reproducible method for determining effective surface area is required. The present investigation will compare the electrocatalytic ability of the nickel whiskers to conventional nickel 200. To measure electrochemical surface area, a low amplitude cyclic voltammetric surface area analysis was employed. This type of analysis will be described specifically for nickel in KOH; however, the technique is not necessarily limited to these conditions.

As an initial procedure, using cyclic voltammetry, the potential of the experimental electrode vs. a calomel reference electrode is varied through a relatively large potential range, from hydrogen evolution to oxygen evolution, in a thirty weight percent KOH electrolyte. The corresponding current passed during the potential sweep between the electrode and the auxiliary counter electrode is monitored. This initial screening step is done in an effort to find a potential range where no reaction is occurring or where there is a minimum of faradaic current. On the current vs. potential plot this criterion corresponds to two parallel lines of low current value when swept in the cathodic and anodic directions, as shown in Figure 2.

Since nickel converts spontaneously to nickel hydroxide when immersed in KOH, it is difficult to

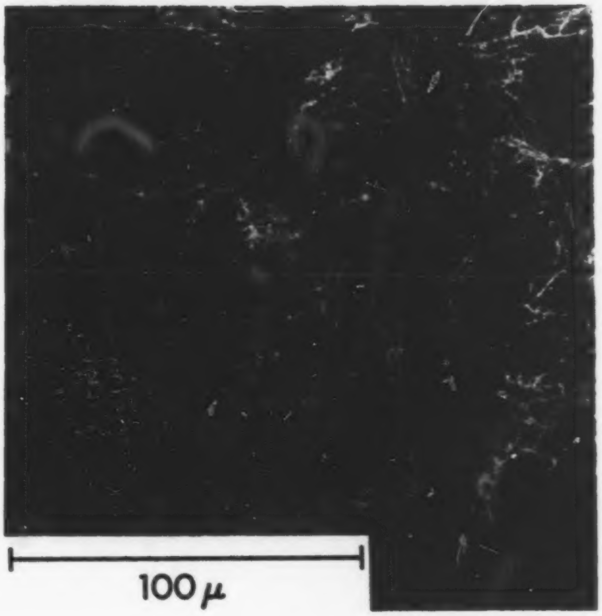


Figure 1. Scanning Electron Micrograph of Whisker Electrode (650x)

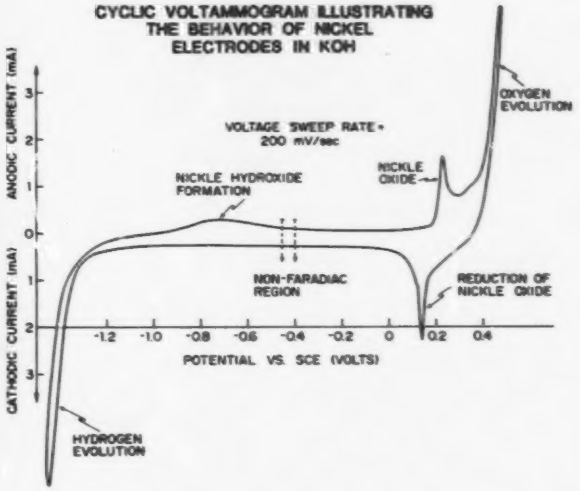


Figure 2

obtain a non-faradaic region on a pure nickel surface in KOH. Even when the nickel is run at a potential cathodic to hydroxide formation in a region where thermodynamically no reaction should occur and nickel hydroxide should be reduced to pure nickel, some faradaic current is observed. Whether this faradaic current is due to impurities, unreduced hydroxide, absorbed hydrogen, or some other unknown reaction has not been determined. Nevertheless, the only apparent non-faradaic region observed for nickel in KOH is in the potential range of -450 mv to -400 mv vs. SCE, which corresponds to a nickel hydroxide surface. This range was chosen for surface area calculations in the present work since it allowed a reproducible set of measurements with reasonable values on polished nickel 200 surfaces.

In a non-faradaic region, the current passed corresponds primarily to the charging and discharging of the electrode surface or double layer. In this region the current vs. potential plot should be a perfect rectangle for a constant sweep rate. The shape of the plot is important because it indicates the presence of a true non-faradaic region in which the relation $C = I/dv/dt$ is valid. This allows measurement of the double layer capacitance (C) and is done by plotting the current vs. potential sweep rate (dv/dt). The slope of this plot is the value of the capacitance, as seen in Figure 3. Once the capacitance of an electrode is found, it can be compared with the standard capacitance of the mercury electrode where no rougheness is assumed. The capacitance value of the mercury electrode is taken as 20 $\mu f/cm^2$. Therefore, if a capacitance value of 40 μf results from a measurement, an active electrochemical surface area of 2 cm^2 is calculated by assuming a specific capacitance of 20 $\mu f/cm^2$. Dividing this area by the apparent geometric surface area gives an idea of the comparative roughness of the electrode surface. The sensitivity of this type of area measurement can be demonstrated by measurements performed on a .005 cm^2 apparent area electrode. Variations in measured surface area due to polishing with various grades of abrasive paper were determined and are shown in Figure 4.

Once the area of an electrode is known to an acceptable level of reproducibility, the electrocatalytic parameters can be determined by the generation of a Tafel plot. The slope of the log current vs. potential voltage plot, and the exchange current density, are the important parameters in determining electrocatalysis. Tafel plots obtained for nickel 200, determined galvanostatically, are quite reproducible. With proper IR compensation, these plots are linear over six decades of current density as calculated using linear regression. A technique has been developed in this laboratory which allows a more precise IR compensation. A typical Tafel plot is shown in Figure 5. Table 1 shows that the average Tafel slope obtained for nickel 200 was 135 mv/decade and the average i_o was equal to 1.2×10^{-6} A/cm^2.

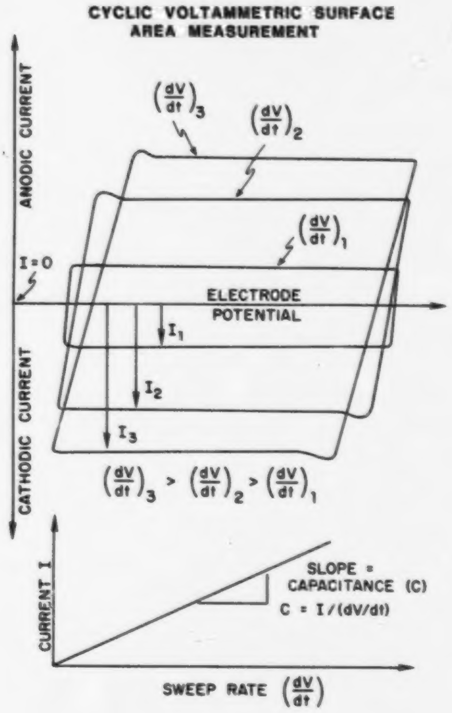
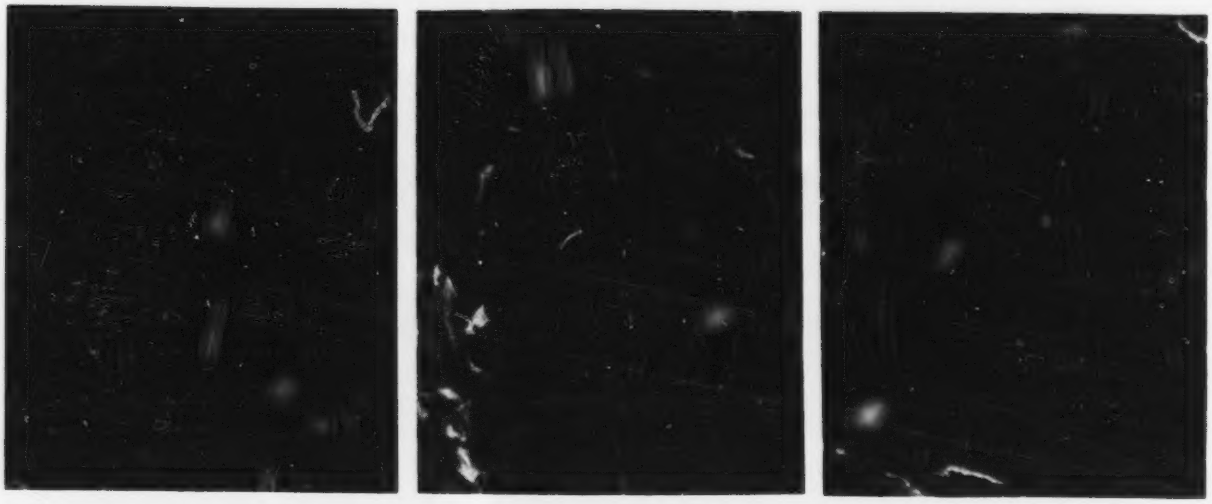

CYCLIC VOLTAMMETRIC SURFACE AREA MEASUREMENT
ANODIC CURRENT
CATHODIC CURRENT
$\left(\frac{dV}{dt}\right)_3$
$\left(\frac{dV}{dt}\right)_2$
$\left(\frac{dV}{dt}\right)_1$
I=0
ELECTRODE POTENTIAL
I_1
I_2
I_3
$\left(\frac{dV}{dt}\right)_3 > \left(\frac{dV}{dt}\right)_2 > \left(\frac{dV}{dt}\right)_1$
CURRENT I
SLOPE = CAPACITANCE (C)
C = I/(dV/dt)
SWEEP RATE $\left(\frac{dV}{dt}\right)$

Figure 3

Now that surface area can be reproducibly measured and the electrocatalytic ability of conventional nickel 200 can be determined with reasonable precision, a comparison with polycrystalline nickel whiskers can be made. It was necessary to make a planar nickel whisker electrode which can be polished smooth and which has no gas masking problems due to porosity. This was accomplished by embedding the nickel whiskers in a epoxy resin and then polishing to a smooth planar surface.

To embed the whiskers, the atmosphere within the pores must be removed to allow the resin to enter. The whiskers are placed on a copper current collector in a teflon mold and held rigidly in place by a magnet. This assembly is then placed within a vacuum system. After the system has been evacuated, a valve to a resin reservoir is opened permitting resin to flow into the mold and embed the whiskers. The resin is outgased in the vacuum for a short time and then cured in an oven at 80° C until completely hard. Once cured, a teflon insulated wire is attached to the current collector, thereby providing electrical connection to the whiskers and making a usable electrode. As seen in Figure 6, the surface of the whisker electrode when polished consists of many small metal islands surrounded by a resin matrix.

Nickel Whisker electrodes of approximately 1 square centimeter true surface area were evaluated for electrocatalytic ability under identical experimental conditions as the conventional nickel 200.



A. Surface polished with alumina slurry, particle size .05μ, surface roughness ~ 3.

B. Surface polished with grit 00 abrasive paper, particle size 30-40μ, surface roughness ~ 4.5.

C. Surface polished with grit 1 abrasive paper, particle size > 60μ, surface area ~ 5.

Figure 4. Scanning Electron Micrographs of Variations in Ni 200 Electrode Surface (2000x).

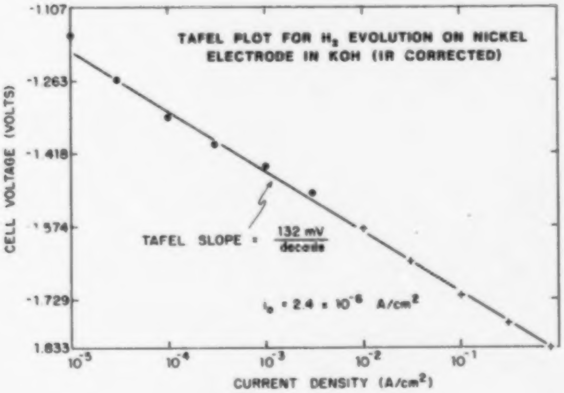


Figure 5

Table 1

NICKEL 200 TAFEL PLOTS*

DATE	TAFEL SLOPE (mv/DECADE)	EXCHANGE CURRENT DENSITY (A/cm^2)	LINEAR FIT (0 - 1)	EXPERIMENTAL CONDITIONS
4/8	130	2.1×10^{-6}	.9930	N_2 PURGE, TEFLON AIR TIGHT CELL, LOW [Fe] KOH, 1/2 HR. EQUILIBRIUM TIME, ~ 1 cm^2 ELECTRODE
4/9	139	1.4×10^{-6}	.9974	
4/10	132	1.1×10^{-6}	.9990	
4/12	135	1.3×10^{-6}	.9753	
4/13	133	1.0×10^{-6}	.9940	
5/29	138	1.2×10^{-6}	.9957	

*EXPERIMENTS RUN APRIL - MAY, 1981.

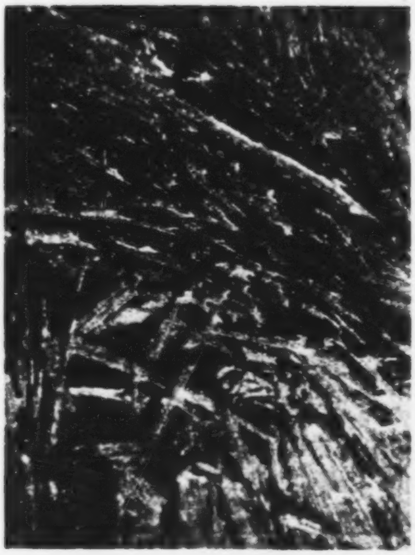


Figure 6. Surface of Whisker-Electrode Embedded in Epoxy Resin Matrix

An average exchange current density of 8.2×10^{-7} A/cm^2 with a average Tafel slope of 133 mv/decade was obtained, as shown in Table 2. Therefore, no significant difference in electrocatalytic ability between the two types of nickel was observed. Annealed nickel 200, which has considerably larger grains and less strain energy than non-heat treated nickel 200 also exhibited essentially the same electrocatalytic properties as those already mentioned. From these evaluations of the electrocatalytic ability of extremely different types of nickel microstructure, it must be concluded that the increased energy of crystal imperfections does little to enhance the hydrogen evolving capabilities of nickel electrodes in KOH. Apparently, current-voltage improvements in alkaline electrolysis using nickel electrodes will be realized mainly by increases in electrode surface area.

HYDROGEN ABSORPTION BY NICKEL ELECTRODES DURING ALKALINE WATER ELECTROLYSIS

An interesting phenomenon was observed while testing for operational stability of both the nickel 200 and nickel whisker electrodes. To insure that the surfaces of the electrodes were not roughening and that no degradation of the epoxy-metal interface was occurring during vigorous hydrogen evolution, low amplitude cyclic voltammetric area measurements were performed following the generation of the Tafel plot. If the electrodes were not stable, a discrepancy between the area measured before and after the Tafel plot would result. Such a discrepancy occurred;

Table 2

NI WHISKER TAFEL PLOTS*

DATE	TAFEL SLOPE (mv/DECADE)	EXCHANGE CURRENT DENSITY (A/cm²)	LINEAR FIT (0 - 1)	EXPERIMENTAL CONDITIONS
SINTERED WHISKERS				
6/15	125	8.4×10^{-7}	.9945	N_2 PURGE, TEFLON AIR TIGHT
6/22	130	9.3×10^{-7}	.9963	CELL, LOW [Fe] KOH, 1/2 hr.
6/10	135	1.2×10^{-6}	.9921	EQUILIBRIUM TIME, ~ 1 cm²
6/4	132	1.3×10^{-7}	.9955	ELECTRODE
FREE WHISKERS				
7/1	141	1.2×10^{-6}	.9932	" "
6/29	136	6.7×10^{-7}	.9954	

*Experiments run June - July, 1981.

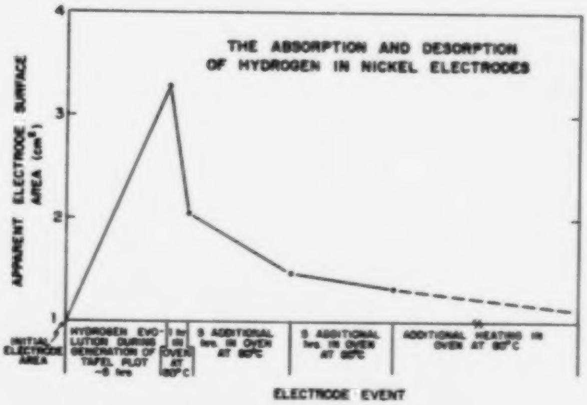


Figure 7

however the data suggest that this was not due to any physical instability of the electrodes.

When hydrogen is evolved on a nickel electrode in KOH, some hydrogen is apparently absorbed into the metal. The absorbed hydrogen changes the specific capacitance or pseudo-capacitance of the nickel as indicated by the current vs. potential plot in the non-faradaic potential region. Instead of being a perfect rectangle symmetric about zero current, the plot is rounded and offset anodically. Surface area measurements calculated from these curves indicate an apparent increase in area by a factor of about 3. The discrepancy in surface area when measured before and after hydrogen evolution diminishes when the hydrogen is forced to diffuse out of the electrode.

Diffusion of hydrogen out of the electrodes can be accomplished by heating an electrode with absorbed hydrogen in an oven at 80° C. The apparent surface area of the electrode is monitored periodically after different periods of heating in the oven. It was found that the apparent area decreased rapidly at first in relation to the amount of time in the oven. The area change then gradually decreased with time to the original value measured prior to the Tafel determination (Figure 7). Hydrogen desorption also occurred at lower temperatures; however, it required longer times than observed in the elevated temperature case. Additionally, when the hydrogen charged electrode was exposed to vacuum ($\sim 10^{-5}$ torr), hydrogen desorption was accomplished at rates similar to the elevated temperature case.

Only this true area, which is totally recoverable by the techniques mentioned above, is used in the current density results reported here. As can be seen in Figure 5, the plots are linear. They are also free of any hysteresis from low current to high current values. Therefore, it is concluded that the hydrogen absorption phenomenon does not effect the comparison of electrocatalytic properties between different crystalline or geometric forms of nickel electrodes.

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RESEARCH ON ADVANCED ELECTROLYTIC HYDROGEN PRODUCTION*

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ABSTRACT

Research on advanced electrolytic hydrogen production consisted of two areas. One was the development of an electrochemical method for investigation of the solid polymer electrolyte (SPE)-electrocatalyst interface, the other was the development of stable photoanodes for photodecomposition of water by coating low barrier n-type semiconductor with a thin film of n-type TiO_2. By using various types of contact electrodes on SPE membranes, it was possible to use modern electrochemical techniques to investigate the SPE-electrocatalyst interface under conditions simulating electrolyzer operation. Low barrier heterojunctions of thin films of n-type TiO_2 on n-type Fe_2O_3 were successfully demonstrated.

INTRODUCTION

SPE-Electrocatalyst Interface: Even though the SPE electrolyzer has been under development for several years, there have been no reports of single electrode measurements on the SPE-electrocatalyst interface using modern electrochemical techniques. Most basic studies on the electrocatalysts and on corrosion of materials in the anode compartment have been carried out in conventional three electrode cells using either aqueous sulfuric acid or trifluoromethansulfonic acid electrolytes. The conditions in these studies may be far removed from those existing in an actual SPE electrolyzer as no measurements of the characteristics of the Nafion/electrode interface have been published. One of the present problems of the SPE electrolyzer is the high electrocatalyst loading. The loading could be reduced if the particle size of the porous catalyst electrode was optimized to offer the maximum area where the gas evolution takes place. These electrochemical reactions may be restricted to the edge of the particles because of limited mass transfer of either oxygen or hydrogen species from the Nafion/catalyst interference to the edges of the catalyst particles. Thus, it is important to carry out measurements under conditions simulating actual operation to determine the locus of the electrochemical reactions, and the influence of the electrocatalyst morphology on the reaction rate.

Photoanodes for Photodecomposition of Water: Since the demonstration by Fujishima and Honda (1) of photodecomposition of water using a TiO_2 anode, there has been considerable research to find a better photoanode material than TiO_2. The large bandgap (3.0 eV) of TiO_2 permits use of only a very small fraction of the solar spectrum. Materials of a lower bandgap are usually unstable in the electrochemical environment. One method of approach has been to coat a material of low bandgap (e.g., GaAs) with a thin film of TiO_2. The idea is to have the TiO_2 film sufficiently thin to transmit the incident light to generate hole-electron pairs in the substrate semiconductor, and to have a sufficiently low barrier at the TiO_2-substrate interface to permit injection of holes to the photoanode surface for the generation of oxygen. All previous attempts to do this either resulted in no hole injection (2,3) or hole injection under an excessively large voltage bias ($\sim$ 2 V SCE) (4). Using available data for the electron affinities for TiO_2 and Fe_2O_3 together with the generally accepted model for heterojunctions (5), it was surmised that a thin film of n-type TiO_2 on an n-type Fe_2O_3 substrate might yield a heterojunction with the desired properties. Accordingly, efforts were focused on the development of a heterojunction consisting of thin coherent films of n-type TiO_2 on n-type Fe_2O_3 substrates.

EXPERIMENTAL

SPE-Electrocatalyst Interface Studies: Figure 1 is a schematic drawing of one version of the cell used for electrochemical studies on the SPE-electrocatalyst interface. This particular cell consisted of a Nafion membrane, a platinum sheet counter electrode, a fused platinum ball contact working electrode, and a calomel reference electrode. Electrolytic contact between the reference electrode and the Nafion electrolyte was made via a Nafion strip "salt bridge." The calomel electrode was used as the reference electrode after other electrodes (e.g., Ag, Ag/Pd and Pd) proved unstable. Apart from the fused platinum ball working electrodes, flat platinum electrodes of various areas were used. In the

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*Work performed under the auspices of the U.S. Department of Energy Contract No. DE-AC02-76CH00016.

latter case, the electrode edges were masked with epoxy. The electrode-membrane assemblies were mounted in a machined polysulfone fixture. The fixture was enclosed in a beaker type cell where the humidity and gas environment could be controlled. Typical measurements that were carried out were cyclic voltammetry, steady state measurements of hydrogen evolution, and investigations of the effect of ambient environment and electrode area on the SPE-electrocatalyst interface.

Photoanodes for Decomposition of Water: The Fe_2O_3 substrates were thermally prepared from 0.025 mm iron foils, by firing them in a Meaker burner flame. The heterojunction electrodes were prepared by chemical vapor deposition (CVD) of ($\sim$ 1200 Å) TiO_2 films on the Fe_2O_3 substrates. Photoelectrochemical characterization of these heterojunctions was carried out in 0.1 N NaOH using standard electrochemical equipment together with a 1000 W Xenon lamp and a monochromator. In addition, the TiO_2 films were characterized using scanning electron microscopy, Auger, XPS and ellipsometric techniques.

RESULTS AND DISCUSSION

SPE-Electrocatalyst Interface Studies: The cyclic voltammetry of a single contact platinum electrode/Nafion interface is shown in Fig. 2 for an area contact of 1.4×10^{-3} cm^2. The curves are similar to those obtained with aqueous sulfuric or trifluoromethanesulfonic aicds. The maximum in the anodic currents around 0.73 V (SHE) result from the reduction of platinum oxide and showed little potential dependence on scan rate. The potential did depend on the maximum potential reached on cycling and the decrease in the potential of the maximum indicated definite interaction with the sulfonic anions even though their mobility is restricted by the polymer chain to which they are bonded.

The current maxima and minima at potentials between 0 and 0.35 V result from the desorption and adsorption of hydrogen atoms in the platinum. The different peaks have been attributed to adsorption isotherm which depend on the crystallographic orientatons of the polycrystalline platinum surface. The amount of charge associated with these adsorption processes have been considered as a measure of the degree of hydrogen coverage on the platinum. Taking a complete coverage as 210 C/cm^2 measurements of the charge was found to give areas a factor of 2-4 times that calculated from the geometric area. These large areas may be associated with the diffusion of hydrogen atoms on the electrode surfaces not in direct contact with the electrolyte. Similar effects were noted on anodizing single contact titanium electrodes on Nafion where interference colors were seen on the surfaces adjacent to but not in contact with the Nafion.

At potentials below 0 V in the current increased rapidly as shown in Fig. 3 as a result of hydrogen evolution. However, the hydrogen evolution currents were limited as shown in Fig. 3 for a slow scan rate of 2 mV/sec in humidified nitrogen. The currents did not increase logarithmically as expected from the hydrogen evolution behavior in aqueous acids and a marked hysteresis was also apparent as the currents were much less cathodic on increasing the potential. This behavior has been found to be high dependent on the pretreatment of the platinum and ambient gas composition. Oxygen markedly increases the effect by increasing the cathodic current and carbon monoxide inhibits it. The increase due to oxygen was far greater than any current contribution around zero potential indicating a marked change in the reactions taking place.

Photoanodes for Photodecomposition of Water: After optimization of the process parameters, both scanning electron microscopy and Auger/XPS studies confirmed the achievement of crack-free TiO_2 films on the Fe_2O_3 substrates. Figure 4 shows current-potential plots for thermally grown Fe_2O_3 electrodes and a CVD TiO_2 electrode on platinum under both dark and illuminated conditions. The results indicate that the respective flatband potentials for the Fe_2O_3 and TiO_2 samples are -0.3 V and -0.7 V SCE. Figure 5 shows a current-potential plot for a TiO_2-coated Fe_2O_3 heterojunction. It can be seen that the heterojunction electrode has the same flatband potential (-0.7 V SCE) as that of CVD TiO_2 on platinum. However, at potentials more anodic than -0.15 V SCE, the slope of the heterojunction curve becomes greater than that of TiO_2 on platinum and approaches that of Fe_2O_3. Figure 6 shows the effect of bias potential on the photoresponse. Increasing the bias from -0.1 V to 0.5 V SCE increases the photoresponse and shifts the peak current to longer wavelength. The fact that the photoresponse starts at about 560 nm for a bias of 0.3 V SCE or greater strongly indicates that there is a hole contribution from the Fe_2O_3 substrate. This heterojunction exhibits the relatively large flatband potential of TiO_2 and the lower spectral threshold of Fe_2O_3. This is the first time that such a low barrier heterojunction has been demonstrated.

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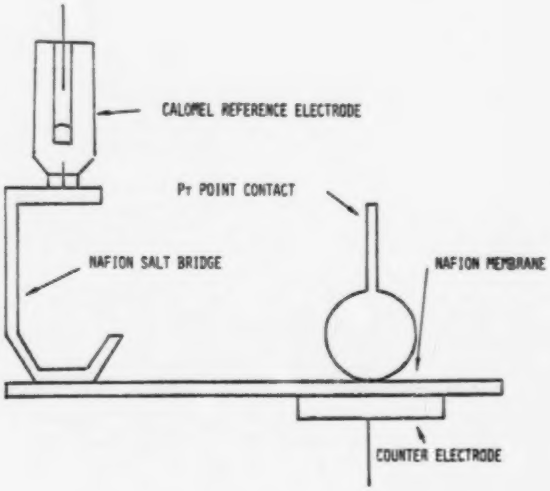
CALOMEL REFERENCE ELECTRODE
Pt POINT CONTACT
NAFION SALT BRIDGE
NAFION MEMBRANE
COUNTER ELECTRODE

Fig. 1. Schematic of Cell for SPE-Electrocatalyst Studies

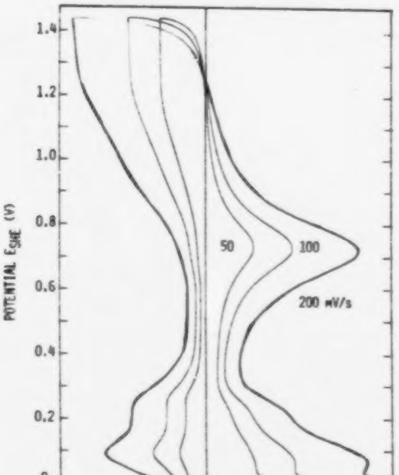

Fig. 2. Cyclic Voltammograms on Pt Electrode in Contact with SPE Membrane

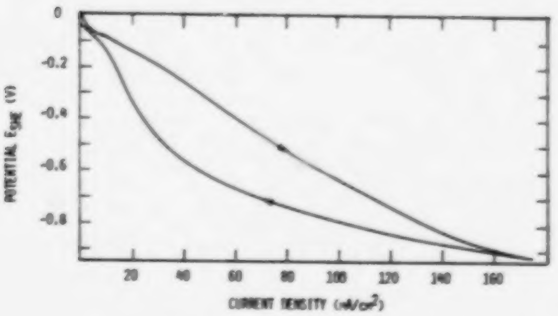

Fig. 3. Current Potential Plots for Pt Electrode in Contact with SPE Membrane

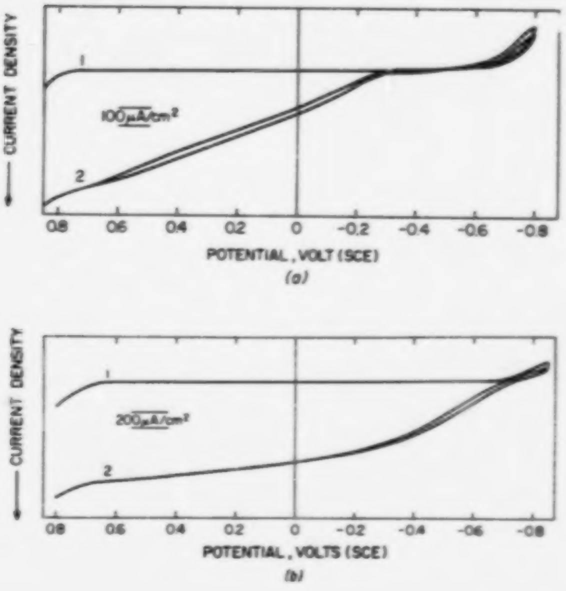

Fig. 4. Current-Potential Curves of (a) Thermally Grown n-Fe_2O_3, and (b) CVD n-TiO_2 Film on a Pt Substrate. Sweep Rate 20 mV/sec; Curve 1, Under Dark; Curve 2, Under Xenon Lamp Illumination of 0.2 W/cm^2

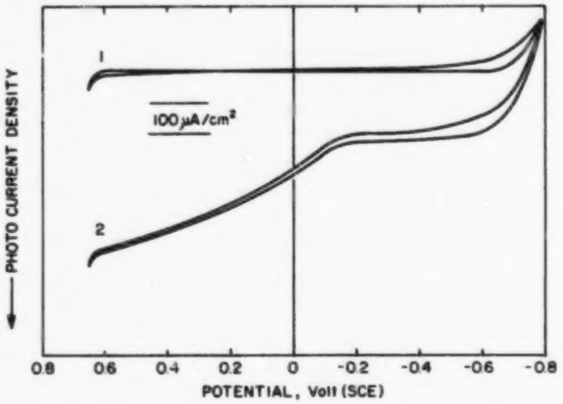

Fig. 5. Current-Potential Curve of the Heterojunction Electrode n-Fe_2O_3/TiO_2. Sweep Rate 20 mV/sec; Curve 1, Under Dark; Curve 2, under Xenon Lamp Illumination of 0.2 W/cm^2

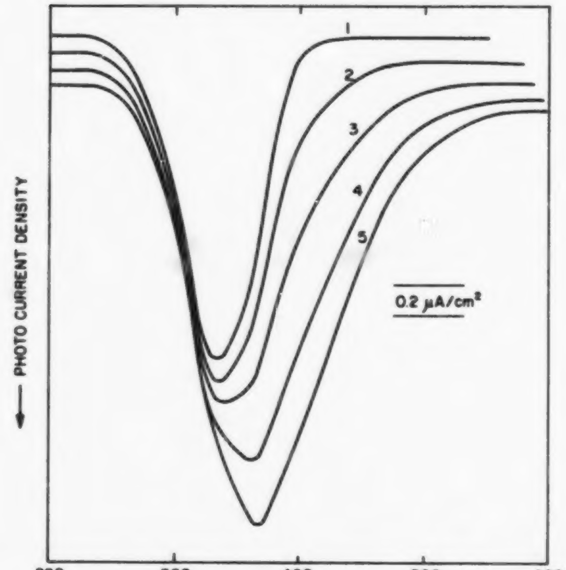

Fig. 6. Photoresponse Spectra of the Heterojunction Electrode n-Fe_2O_3/TiO_2 at Different Bias Potential. Curve 1, -0.1 V; Curve 2, 0.0 V; Curve 3, 0.1 V; Curve 4, 0.3 V; Curve 5, 0.5 V vs SCE. Xenon Lamp Illumination Set at 0.1 W/cm^2 Before Insertion of Monochromator

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HYDROGEN PRODUCTION (Thermochemical)

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PROJECT SUMMARY

Project Title: Thermochemical Water-Splitting Program

Principal Investigator: G. E. Besenbruch

Organization:

General Atomic Company
General Programs Division
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Project Goals: This program involves experimental research and development of the Sulfur/Iodine thermochemical water splitting cycle. Specific objectives include improvement of the critical chemistry aspects of the process, development of a bench-scale unit which evaluates the major aspects of the cycle, and development of engineering flowsheets for estimation of process costs and efficiency. Funding on solar and fusion applications of the process is provided by DOE Solar Thermal Power Office and the DOE Office of Fusion Energy.

Project Status: Operation of the bench-scale unit (Sections I and III) resulted in modifications to the system. Operation of Section I (Main Solution Reaction) was substantially simplified by developing an automatic phase separator. The lower phase purification system (Section III) was modified to incorporate automatic bottoms removal in the $HI/I_2/H_3PO_4$ distillation section. The problem of liquid iodine transport was finally resolved with the development of a liquid iodine pump. A detailed process cost estimate was initiated. Flowsheet Section I (Main Solution Reaction) has a 40% lower cost than a less detailed JPL estimate. Preliminary data indicate that the cost for Section IV (HI Decomposition) is similar to the JPL estimate. A new process which may eliminate the phosphoric acid extraction step of Section III (HI_x Purification) is under development. This concept would greatly decrease the capital cost of Section III.

Contract Number: DE-AC02-08ET26225

Contract Period: October 1980 - September 1981

Funding Level:

400,000	DOE STOR	(FY-1981)
50,000	DOE SOLAR	(FY-1981)
80,000	DOE Fusion	(FY-1981)
80,000	Utility Funding	(CY-1981)
80,000	GA Contribution	(CY-1981)

Funding Source:

Department of Energy - STOR
Department of Energy - Solar Thermal Power Office
Department of Energy - Office of Fusion Energy
General Atomic Company
Several utilities
Gas Research Institute

THE SULFUR-IODINE THERMOCHEMICAL WATER-SPLITTING CYCLE

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ABSTRACT

Major process improvements which had been identified in an earlier phase of this program were investigated and their feasibility demonstrated. The engineering process flowsheet was revised to incorporate the newest process improvements. It is now being used for an estimate of hydrogen production cost from the GA cycle. A potential system for HI purification was investigated which could eliminate the need for the present pHosphoric acid treatment completely and would result in significant savings in capital cost for this part of the process. Potential catalysts for the liquid HI decomposition step were evaluated. Noble metals appear to have highest activity, however, attrition of the catalyst occurs.

INTRODUCTION

The sulfur-iodine thermochemical water-splitting cycle presents an alternate concept for the production of hydrogen. Its high thermal efficiency (47%) make it particularly attractive for solar applications since the size of the mirror field is directly proportional to the process thermal efficiency. This could result in significantly lower overall plant cost for a process with higher thermal efficiency. General Atomic Company has been working on this cycle since 1974. The main goal for the development effort has been to demonstrate the feasibility of the concept and to improve the system to the state where it can be competitive as an alternate hydrogen production process in the future. The major effort over the last year has been to identify and develop concepts which would increase the efficiency and decrease the capital cost of this process. The testing and operation of a bench-scale system has been a valuable tool in this work.

PROCESS DETAILS

Bench-Scale

The equipment of Section III (Hydrogen Iodide (HI) Purification and Decomposition) which had been previously installed, was operated successfully. A major part of the effort was expended in modifying the equipment to improve operability, increasing throughput, and gathering process data during operation.

The HI separation column and H_3PO_4 concentration columns were modified to increase boilup rate and thus throughput. High throughput rates of viscous H_3PO_4 resulted in flooding of the columns. The separation efficiency decreased when the flooding was eliminated through the use of larger packing in the columns. Plate type columns have been ordered, which will eliminate this problem.

The hydrogen iodide cracker was operated with no major problems from the beginning. A conversion ($2HI \quad H_2 + I_2$) of 22% per pass has been routinely obtained. The predicted equilibrium conversion at the measured reactor outlet temperature is 16%. This discrepancy has not been fully explained yet. It is believed that there is temperature maldistribution at the reactor inlet which, if propagated, could give the observed result. Efficient iodine removal from the product stream was achieved by increasing the heat transfer area of the iodine trap and by lowering the temperature. Glass HI traps were replaced with stainless steel pressure vessels allowing longer run times and better control of the recycle HI flow.

The iodine knock-out portion of Section III has been moved closer to the Section I prime reactor to allow short circuit return of the separated iodine. In the new location, the equipment is placed in a "hot box" for improved temperature control. In addition, better use of fluid density differences to obtain self automation of process flows was made.

Engineering

The flowsheets for Sections I, III, and IV were revised. These revisions are the basis for a hydrogen production cost estimate which is now being carried out at GA. Preliminary indications are that the cost of hydrogen from the GA thermochemical water-splitting process using solar heat as the energy source is in the range of $12-$20 per MBtu depending on the cost of solar heat. These numbers compare very well with an earlier cost estimate published by K. Ekman of JPL.

PRELIMINARY COST ESTIMATE FOR GA PROCESS
(400 MW(th) SOLAR PLANT)

	SECTION	EKMAN (JPL) * $ (X10^6)	GAC $ (X10^6)
I.	Main Solution Reaction	54	28
II.	H_2SO_4 Decomposition	100	Not Done Yet
III.	HI Purification	167	162
IV.	HI Decomposition	14	16
V.	Power Generation and Heat Transfer	47	Not Done Yet

* Reduced to 400 MW(th).

Process Chemistry

The processing of the lower phase HI solution, high in iodine and containing significant amounts of H_2O, is a critical step in the GA sulfur-iodine water-splitting cycle because of its potentially high cost. At present, the recovery of HI is accomplished by adding concentrated H_3PO_4 such that the final H_3PO_4-H_2O solution exceeds 85% H_3PO_4. In doing so, two things happen:

1. Much of the excess I_2 separates as a second liquid phase.
2. The HI is increased in chemical activity while the H_2O activity is decreased and the HI can be distilled out of this mixture at superazeotropic conditions such that the distilled HI can be recovered as a dry liquid.

While H_3PO_4 accomplishes the necessary steps, it requires a considerable H_3PO_4 recycle flow, also, the energetics for removing the H_2O from the H_3PO_4 are demanding. At present, this is done quite efficiently by the use of compressive work, but the equipment in the form of heat exchangers and vapor recompression turbines is quite expensive.

Research has been carried out to investigate other methods of processing the HI_x product solution. We were successful in identifying a potentially very attractive process which can accomplish the necessary separations. The advantage of this concept is in the fact that no phosphoric acid treatment is required and that the amount of water that needs to be evaporated is only a fraction of the old flowsheet value. Patent protection is being sought for this new process improvement. However, there are still a number of process details that need to be investigated before the system can be adopted as an alternate for HI_x product solution purification.

LIQUID HYDROGEN IODIDE CATALYST STUDIES

During the past years, General Atomic has studied the advanced concept of decomposing HI in the liquid phase. Theoretical calculations had indicated that high conversions were possible. Experiments conducted in glass pressure vessels under restricted pressure and temperature conditions and batch operation showed great promise for the use of the method in the sulfur-iodine cycle. Measured conversion values were comparable to the high values predicted theoretically, and reaction rate data, extrapolated to higher process temperatures, indicated that application of the system to the GA cycle would result in a viable process. In order to evaluate this concept under anticipated process conditions, a system was designed, constructed, and operated in which the decomposition of liquid HI at high temperatures and pressures and flow conditions leading to reasonable reactor residence times could be investigated. In addition, some batch studies were performed in parallel in an attempt to evaluate catalyst stability in the liquid HI environment.

Two major conclusions can be drawn from the work performed to date. First, noble metal catalysts provide the highest rates of decomposition and second, there is significant attrition of noble metal into the liquid HI environment. The cost involved in using noble metal catalysts for this process were not found to be excessive. Also, catalyst recovery is common in the chemical industry. Therefore, catalyst attrition is not expected to be a problem in the process. We are also pursuing a new, very attractive scheme for catalyst recycle which does not involve total catalyst recovery and regeneration.

PROJECT SUMMARY

Project Title: Alternate Thermochemical Cycles

Principal Investigator: Charles M. Hollabaugh and Melvin G. Bowman

Organization:

Los Alamos National Laboratory
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FTS 843-5813, 843-6014

Project Goals: Provide experimental and/or analytical support for sulfuric acid cycles selected for process development by Chemical and Hydrogen Energy Systems, U. S. Department of Energy. More specifically, our goals are to:

1. conduct research on solid sulfates and oxides which may serve as alternatives for the sulfuric acid cycles,
2. evaluate methods for handling solids in practical systems, and
3. analyze the interfacing of cycles with fission, fusion, and solar heat sources.

Project Status: Basic thermochemistry studies have been completed for two different steps in the decomposition of bismuth sulfate. Two different bismuth sulfate cycles have been defined for different sulfuric acid strengths. The eventual "best" cycle will depend on energy required to form sulfuric acid at different concentrations.

A rotary kiln has been used in experiments to decompose $Bi_2O(SO_4)_2$, $La_2(SO_4)_3$, $ZnSO_4$, and Co_3O_4. Over 90% decomposition of all but $La_2(SO_4)_3$ is obtained at temperatures below 1285 K with a residence time of 60 s. Higher temperatures are required for $La_2(SO_4)_3$ decomposition.

In our fluid bed, the fraction of $ZnSO_4$ that decomposes in less than 1.0 s residence time varies with the feed rate. At a feed rate of 4.0 m mol/min, 85% decomposes at 1223 K. At a higher rate of 19 m mol/min, only 48% decomposes.

The heat requirements for decomposing H_2SO_4 and $Bi_2O(SO_4)_2$ were compared and evaluated relative to the heat delivery characteristics of a gas cooled reactor. While H_2SO_4 is well suited for a gas cooled reactor, $Bi_2O(SO_4)_2$ is better suited to an isothermal heat source such as a solar furnace.

Contract Number: A1-10-05-15-0

Contract Period: October 1, 1980 through September 30, 1981

Funding Level: $150,000

Founding Source:

Chemical/Hydrogen Energy Systems
U. S. Department of Energy

ALTERNATE THERMOCHEMICAL CYCLES

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ABSTRACT

Experimental verification of all steps in the bismuth sulfate cycle has been obtained. At acid concentrations greater than 52.7 wt%, normal $Bi_2(SO_4)_3$ is formed but at lower concentrations, greater than 3.0 wt%, the bismuth oxysulfate, $Bi_2O(SO_4)_2$, is formed. Upon heating to temperatures in the range of 975 to 1150 K, both decompose by the loss of SO_3 to a final composition of $Bi_2O_{2.3}(SO_4)_{0.7}$. The higher sulfates are regenerated by reaction of this product with H_2SO_4.

Solids handling and decomposition have been studied in a laboratory-scale rotary kiln and a dual-particle fluidized bed. Kiln experiments with $Bi_2O(SO_4)_2$, $ZnSO_4$, and Co_3O_4 have shown that in temperature range of 1125 to 1285 K, over 90% decomposition occurs during the 60 s residence time. A higher temperature is required for $La_2(SO_4)_3$ decomposition. A dual-particle fluidized bed was constructed and tested with $ZnSO_4$ powder. Even with the short residence time of less than 1.0 s, over 50% decomposition is obtained at a temperature greater than 1223 K.

Cycles based on solids decomposition matches the thermal characteristics of an isothermal heat source in contrast to the H_2SO_4 cycle which best fits the heat delivery characteristics of a gas cooled reactor. A comparison has been made of the heat requirements for both H_2SO_4 and $Bi_2O(SO_4)_2$ decomposition and the results evaluated relative to the load line of a gas cooled reactor.

INTRODUCTION

Our work comprises three areas of interest: the bismuth sulfate cycles, solids handling and decomposition, and comparison of the heat requirements for the decomposition of H_2SO_4 and $Bi_2O(SO_4)_2$. This report summarizes the status of these studies.

BISMUTH SULFATE CYCLE

We have completed studies of the thermochemistry of bismuth sulfate decomposition and determined that bismuth sulfate decomposes through a series of intermediate oxysulfates rather than directly to bismuth oxide. Equations 1, 2, and 3 illustrate this progressive decomposition.

$$Bi_2(SO_4)_3 = Bi_2O(SO_4)_2 + SO_3 \tag{1}$$

$$Bi_2O(SO_4)_2 = Bi_2O_2SO_4 + SO_3 \tag{2}$$

$$Bi_2O_2SO_4 = Bi_2O_{2.3}(SO_4)_{0.7} + 0.3\ SO_3 \tag{3}$$

Enthalpies for reactions 1 and 2 were determined experimentally by measuring equilibrium gas pressures as a function of temperature. The values obtained are 161 and 172 kJ/mol for reactions 1 and 2, respectively. Although the enthalpy for reaction 3 was not determined, it is expected to approximate that for reaction 2 since the decomposition proceeds rapidly to the bismuth oxysulfate product of reaction 3.

We found that $Bi_2O(SO_4)_2$ is the stable sulfate in contact with sulfuric acid in the concentration range of 3.0 to 52.7 wt% at ambient temperature. This oxysulfate contains three waters of hydration. At acid concentrations higher than 52.7 wt%, the stable sulfate is $Bi_2(SO_4)_3$ with no waters of hydration. From our studies it is clear that there are two alternate bismuth sulfate cycles based on the initial formation of sulfuric acid. These alternates are outlined below:

Alternate 1

$$Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ H_2SO_4 = Bi_2(SO_4)_3 + 2.3\ H_2O \tag{4}$$

$$Bi_2(SO_4)_3 = Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ SO_3 \tag{5}$$

Alternate 2

$$Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ H_2SO_4 = Bi_2O(SO_4)_2 + 1.3\ H_2O \tag{6}$$

$$Bi_2O(SO_4)_2 = Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ SO_3 \tag{7}$$

Both alternates contain an additional step for the decomposition of SO_3 to SO_2 and O_2.

Alternate 1 requires higher strength sulfuric acid, but for each mol of SO_3 finally decomposed, it requires a lower bismuth inventory and less energy for drying the solid sulfate. Alternate 2 requires lower strength sulfuric acid. Thus, its potential advantage depends on the possibility that significantly less energy may be required to form dilute sulfuric acid. Studies to determine the energy required to form sulfuric acid as a function of concentration are being made in other programs, primarily in other laboratories.

ROTARY KILN

A laboratory-scale rotary kiln was constructed from a 25-mm diameter quartz tube which is coupled to a screw feeder through a gas tight rotary seal. Fig. 1 is a schematic of this system. This rotary kiln was used in experiments to decompose $Bi_2O(SO_4)_2$, $La_2(SO_4)_3$, $ZnSO_4$, and Co_3O_4. Results for these experiments are presented in Fig. 2 and Table 1.

The decomposition of $Bi_2O(SO_4)_2$ occurs rapidly at temperatures of 1073 and 1123 K with more than 90% decomposing during the 60 s residence time. At temperatures higher than 1150 K, problems were encountered with caking and reaction with the quartz tube. Both $ZnSO_4$ and Co_3O_4 decompose readily in the kiln with over 90% decomposing at 1283 K. A higher temperature is required to decompose $La_2(SO_4)_3$.

DUAL PARTICLE FLUIDIZED BED

A dual particle fluidized bed was constructed and tested. In this system, a bed of spherical particles of ZrO_2 approximately 450 micrometer diameter, is fluidized with argon. The argon also serves as a carrier gas to transport the powder to be decomposed to and through the bed. A screw feeder is used to meter the powder. The decomposed material is collected down stream in a cyclone separator. Fig. 3 is a schematic of the system.

The results of our initial studies with $ZnSO_4$ are presented in Fig. 4. The decrease in the fraction decomposed with increasing feed rate reflects two possible effects. The first is the increase in partial pressure of SO_3 which would tend to slow down the reaction, but the partial pressure of SO_3, assuming that all the active gas is SO_3 and none has decomposed to SO_2, is less than 0.1 atm even at the highest rate and we believe that the inhibiting effect on the reaction rate is minor. The other is an effect due to heat transfer to the bed and this seems to influence the reaction rate to a large degree but a more detailed study is needed to evaluate this effect.

MATCHING CYCLES WITH THERMAL ENERGY SOURCES

Cycles based on solid decomposition almost require a source of high temperature isothermal heat rather than heat from a circulating gas cooled reactor. In contrast, sulfuric acid cycles are better suited for heat delivered from a cooling gas stream. Of course an isothermal heat source can be used for sulfuric acid cycles, but with a loss of efficiency of the very high temperature heat.

The heat requirements versus temperature for H_2SO_4 and $Bi_2O(SO_4)_2$ decomposition are given in Tables 1 and 2, respectively. The heat required for drying H_2SO_4 is not included. The heat values for H_2SO_4 were obtained by summation from 700 K all the heat needed to vaporize the acid and to dissociate the gases to yield 1.0 mol of SO_2 at 1300 K and 10.6 atm. This heat could be supplied by cooling 22.5 mol of helium from 1325 to 725 K as shown in Fig. 5. Similarly the heat requirements for $Bi_2O(SO_4)_2$ were calculated starting at 1125 K. In this case more helium is required because of the smaller temperature range for cooling, 1325 to 1150 K. Therefore, it requires 81 mol of helium to produce 1.0 mol of SO_2 at 1300 K.

The H_2SO_4 decomposition requirements closely match the load line curve for a gas cooled reactor. In contrast, the heat requirements for $Bi_2O(SO_4)_2$ are mostly at a single temperature and do not match the characteristics of the gas cooled reactor and, consequently, would be better suited to an isothermal heat source such as a solar furnace.

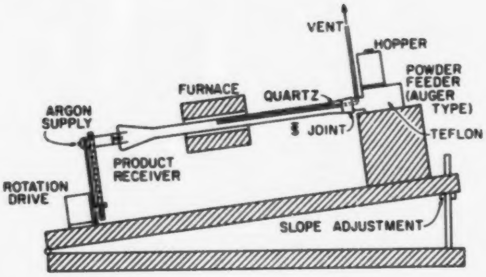
VENT
HOPPER
POWDER FEEDER (AUGER TYPE)
FURNACE
QUARTZ
ARGON SUPPLY
$ JOINT
TEFLON
PRODUCT RECEIVER
ROTATION DRIVE
SLOPE ADJUSTMENT

Fig. 1. Laboratory rotary kiln system.

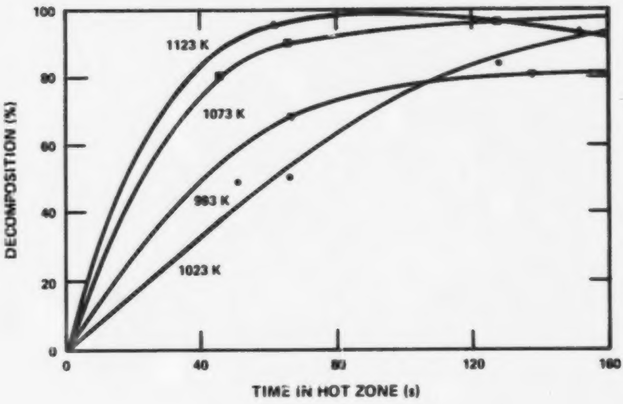

Fig. 2. $Bi_2O(SO_4)_2$ decomposition in rotary kiln.

TABLE 1

SOLIDS DECOMPOSITION IN ROTARY KILN

Solid	Temp (K)	Time (s)	Decomp (%)
$La_2(SO_4)_3$	1283	66	11.5
$ZnSO_4$	1223	60	45.6
	1283	60	92.1
Co_3O_4	1283	60	100

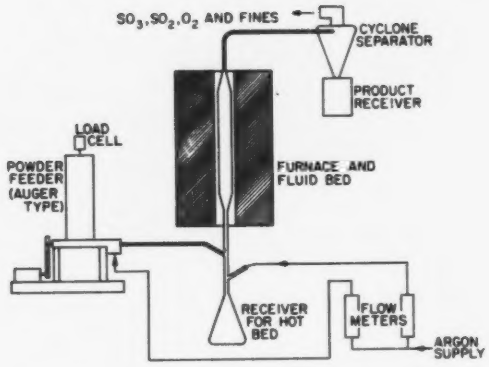
SO_3, SO_2, O_2 AND FINES
CYCLONE SEPARATOR
PRODUCT RECEIVER
LOAD CELL
POWDER FEEDER (AUGER TYPE)
FURNACE AND FLUID BED
RECEIVER FOR HOT BED
FLOW METERS
ARGON SUPPLY

Fig. 3. Dual-particle fluidized bed system.

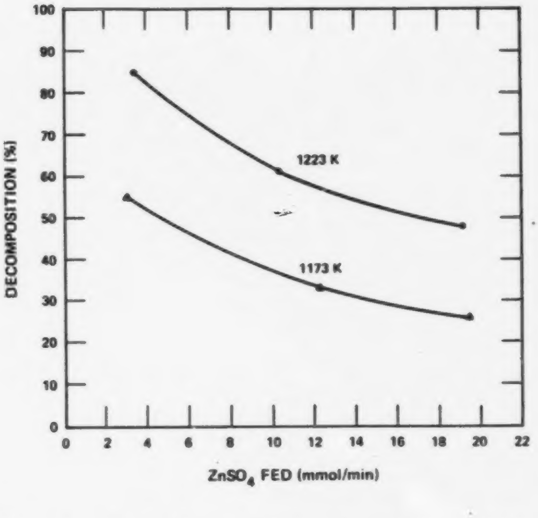

Fig. 4. $ZnSO_4$ decomposition in the fluid bed.

TABLE 2

HEAT REQUIREMENTS FOR THE DECOMPOSITION OF H_2SO_4

Temp (K)	Cumulative Heat (kJ)
700	113.6
900	194.2
1100	248.4
1300	280.1

At equilibrium, 1.17 mol H_2SO_4 yields 1.0 mol SO_2 at 1300 K. Heat can be supplied with 22.5 mol He cooled from 1325 to 725 K.

TABLE 3

HEAT REQUIREMENTS FOR THE DECOMPOSITION OF $Bi_2O(SO_4)_2$

Temp (K)	Cumulative Heat (kJ)
1125	270.4
1200	283.2
1300	293.9

At equilibrium, 1.14 mol $Bi_2O(SO_4)_2$ yields 1.0 mol of SO_2 at 1300 K. Heat can be supplied with 81 mol of He cooled from 1325 to 1150 K.

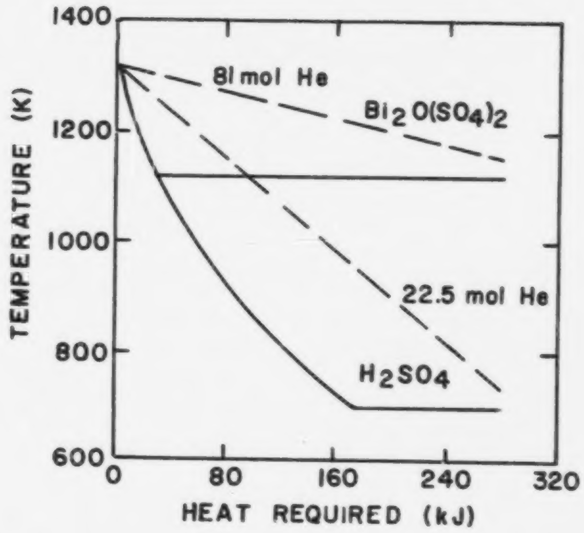

Fig. 5. Simplified load line curves for gas cooled reactor and heat of decomposition of H_2SO_4 and $Bi_2O(SO_4)_2$.

SOLUBILITY OF SULFUR DIOXIDE IN SULFURIC ACID

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Pasadena, California 91103

ABSTRACT

The solubility of sulfur dioxide in 50% (wt./wt.) sulfuric acid was evaluated by regular solution theory, and the results verified by experimental measurements in the temperature range of 25°C to 70°C at pressures of 60 to 200 PSIA. The percent (wt./wt.) of sulfur dioxide in 50% (wt./wt.) sulfuric acid is given by the equation $\%SO_2 = 2.2350 + 0.0903P - 0.00026P^2$ with P in PSIA.

INTRODUCTION

There are five thermochemical water splitting cycles that have been extensively investigated (see notes). They all have in common sulfur dioxide and sulfuric acid as part of the cycle in concentration ranges of 50 to 60%. Laboratory bench scale units have been assembled and in all cases operated at ambient pressures. In any large scale-up to practical commercial units the process pressures must be increased so that:

1. Gains in process efficiencies can be achieved.
2. The hydrogen and oxygen can be produced at high pressures to avoid the costs of pumping.

On review of the literature very little data exists on the solubility of sulfur dioxide in sulfuric acid (1,2,3). All of these data are at low pressures of sulfur dioxide in sulfuric acid, and the data given by Simeck et. al. was shown to follow Henry's Law (3). Because of the importance of this information we have calculated the solubility of sulfur dioxide in 50% (wt./wt.) sulfuric acid. To verify these calculations, measurements of the solubility of the gas in the acid were undertaken in the temperature range of 25°C to 70°C at pressures of 60 to 200 PSIA.

MISCIBILITY OF LIQUID SYSTEMS

In general, solubility, or miscibility of two liquids, is to be expected if there is a decrease in the free energy of mixing, i.e..

$$\Delta F_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{1}$$

Inasmuch as the entropy of mixing ΔS_{mix} is always positive (i.e., $- T\Delta S_{mix} < 0$), the enthalpy of mixing ΔH_{mix} will virtually determine solubility. The latter term for non-polar and some polar substances is positive and its magnitude is proportional to the difference of the respective solubility parameters, δ, which are the square roots of the cohesive-energy densities.

$$\Delta H_{mix} \cong (\delta_1 - \delta_2)^2 \tag{2}$$

Thus, the closer the solubility parameters values, the smaller ΔH_{mix} will be and, consequently, the greater the decrease in ΔF_{mix}.

For the condition of liquid immiscibility the following approximation was obtained by Hildebrand and Scott (4).

$$\Delta H_{mix} \cong V (\delta_1 - \delta_2)^2 > 2RT \tag{3}$$

If an approximation is made for V by using the arithmetic mean of V_1 and V_2 when $V_1 \neq V_2$, then the expression becomes:

$$\frac{1}{2}(V_1 + V_2)(\delta_1 - \delta_2)^2 > 2RT \tag{4}$$

$$Q = \frac{1/2\ (V_1 + V_2)\ (\delta_1 - \delta_2)^2}{2RT} \tag{5}$$

If the quotient Q is greater than 1, then the inequality of Equation 4 is satisfied and the liquids are immiscible.

These equations or approximations are to be regarded as a first order estimation or guide in the determination of miscibility of a system and should be experimentally verified if practical.

An estimation of the miscibility of sulfur dioxide (50% (wt./wt.)-sulfuric acid as per Equation (5) at 25°C (298K) is obtained from the results of the calculations shown in Equation 6):

$$Q = \frac{1/2\ (46.79 + 35.67)\ (20.80 - 10.75)^2}{2 \times 1.986 \times 298} = 3.25 \tag{6}$$

Evaluation of terms in Equation 6 is shown in Table 1. The calculated value of Q in Equation 6 exceeds 1. Therefore sulfur dioxide is not completely miscible in 50% (wt./wt/) sulfuric acid. Figure 1 is a photograph of a two-phase-liquid system using the 50% H_2SO_4. For concentrated sulfuric acid the calculated value of Q is 2.31. This result suggests that sulfur dioxide is more soluble in concentrated sulfuric acid.

Table 1. Values of Solubility Parameters and Molar Volumes

Material	Solubility Parameter, δ	Molar Volume, V cc/g-mole	Remarks
H_2SO_4 (25°C)	18.14	53.28	δ calc'd from vapor pressure data (5)
SO_2 (25°C)	10.75	46.79	δ calc'd from Antoine equation constants (5)
H_2O	23.46	18.069	δ calc'd as above (5)
H_2SO_4-H_2O 50% (wt./wt.)	20.80	35.67	δ calc'd by the method of Gjaldbaek (6)

EXPERIMENTAL

The volume of the glass ampule used in this experiment was first calibrated with known amounts of water. Then a known quantity of 50% sulfuric acid was placed in the ampule along with a magnetic stirring bar. Sulfur dioxide was subsequently condensed into the ampule at liquid nitrogen temperature, and the ampule was sealed. The system was slowly heated and allowed to come to equilibrium at each measurement temperature. Care was exercised to avoid the formation of emulsions. The experimental apparatus is shown in Figure 2.

A quadratic regression analysis performed on the data gave the following equation

$$\%\ SO_2 = 2.2350 + 0.0903P - 0.00026P^2 \tag{7}$$

where P is the vapor pressure of sulfur dioxide from 60 to 200 psia (Figure 3).

CONCLUSION

The results show that the solubility of sulfur dioxide in sulfuric acid deviates from Henry's Law at higher pressures (Figure 3) (3).

ACKNOWLEDGMENT

The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, and was supported by the Department of Energy through an agreement with NASA.

NOTES

1. The General Atomics Sulfur-Iodine cycle is described by:

$$SO_2 + 2H_2O + I_2 \rightarrow H_2SO_4 + 2HI$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2} O_2$$

$$2HI \rightarrow H_2 + I_2$$

2. Ispra Mark 16 cycle is conceptually the same as the General Atomic cycle.

3. The Westinghouse Hybrid Sulfuric acid cycle is represented by:

$$SO_2 + H_2O \rightarrow H_2SO_4 + H_2 \text{ by electrolysis}$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2} O_2$$

4. The Ispra Mark 11 cycle is conceptually the same as the Westinghouse Hybrid cycle.

5. A prepresentation of the Ispra Mark 13 Sulfur-Bromide Hybrid cycle is given by the following:

$$SO_2 + 2H_2O + Br_2 \rightarrow H_2SO_4 + 2HBr$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2} O_2$$

$$2HBr \rightarrow H_2 + Br_2 \text{ by electrolysis}$$

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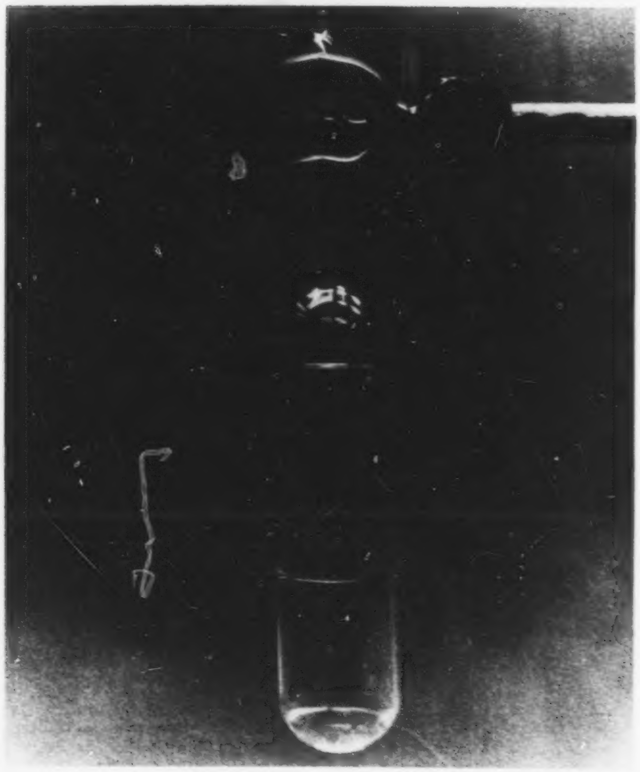

Figure 1. Sulfuric acid (50% wt./wt.) and liquid sulfur dioxide. The top phase is sulfur dioxide and bottom phase is the acid.

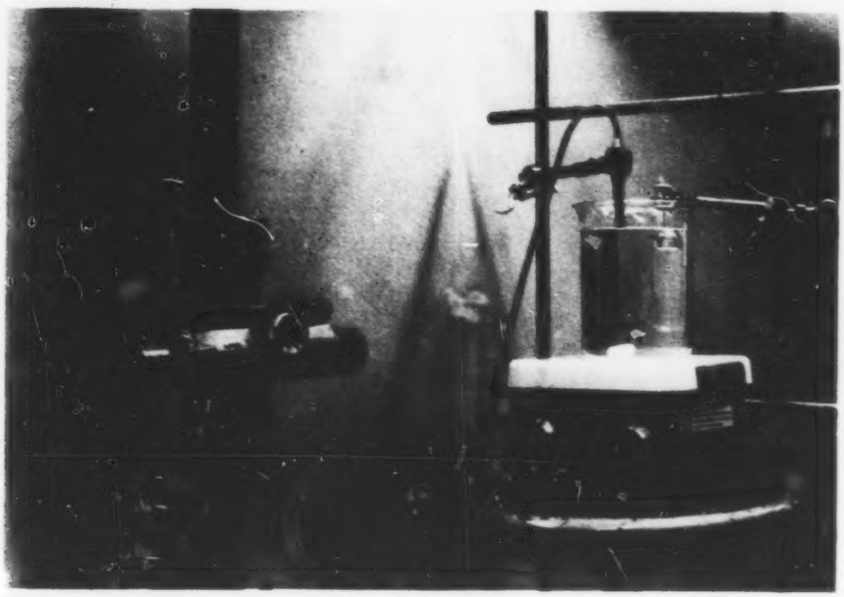

Figure 2. Experimental apparatus for measuring solubility of sulfur dioxide in sulfuric acid. The Gaertner cathetometer is accurate to ±0.005 cm. Temperatures were measured to ±0.01°C with a Dymec quartz thermometer.

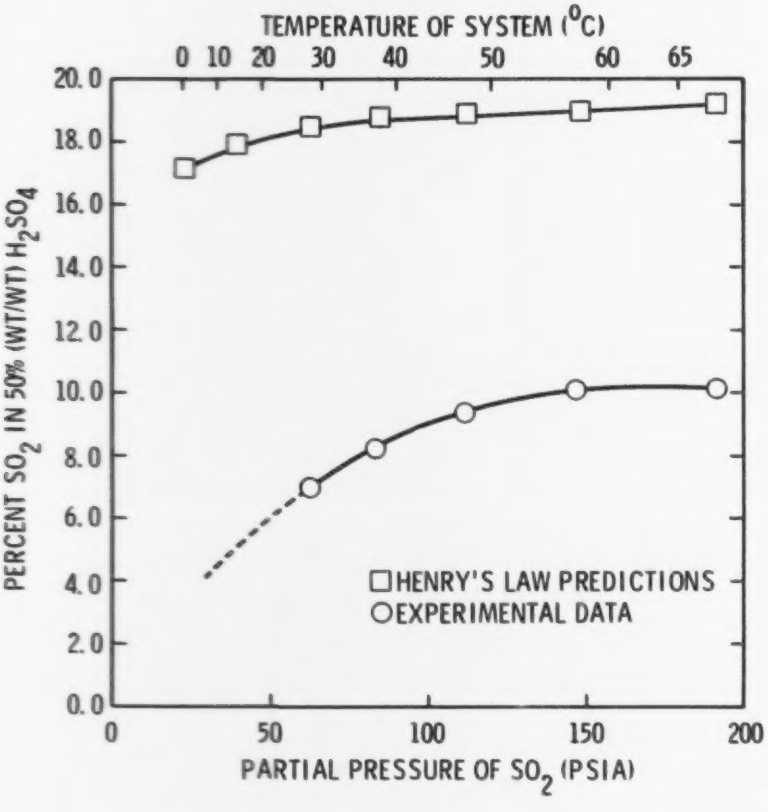

Figure 3. The solubility of sulfur dioxide in (50% wt./wt.) in sulfuric acid.

HYDROGEN STORAGE/RECOVERY

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PROJECT SUMMARY

Project Title:	The Effects of Hydrogen on Low-Cycle-Fatigue Life and Slow Crack Growth in Pipeline Steels
Principal Investigator:	John H. Holbrook
Organization:	Battelle, Columbus Laboratories Physical Metallurgy Section Columbus, Ohio 43201
Project Goals:	Investigate enhancement of fatigue-crack-growth rate by hydrogen gas in representative line-pipe steels as a function of hydrogen pressure, cyclic frequency, and cyclic load magnitude. Establish whether sustained-load slow-crack growth is likely to occur in steel pipelines and welds transporting hydrogen.
Project Status:	Activity on contract commenced in mid-July, 1981. The program is designed to investigate enhancement of both fatigue and static-load crack growth in line-pipe steels by hydrogen gas. Both of these crack-growth phenomena will be studied with laboratory tests on standard fracture mechanics-specimens. Hydrogen-enhanced fatigue-crack growth will also be studied using internally flawed pipe sections. Efforts thus far in both laboratory testing and pipe testing have been on material procurement and configuring and checking out testing apparatus. The first laboratory tests are planned for mid-November, 1981. The first pipe section tests are planned for late October, 1981.
Contract Number:	BNL 550722-S
Contract Period:	June 10, 1981 through June 10, 1982
Funding Level:	$164,650
Funding Source:	U. S. Department of Energy through Brookhaven National Laboratory

HYDROGEN COMPATIBILITY OF STEELS

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ABSTRACT

Hydrogen-induced subcritical-crack growth and hydrogen-enhanced fatigue-crack growth in steel pipelines and weldments appear to be the most serious material problems to overcome if the underground natural gas pipeline system is to be used for hydrogen transport. The hydrogen compatibility of in-line compressors on the system is unknown at this time but could also be a cause for some concern.

INTRODUCTION

For hydrogen to represent a viable energy source for widespread consumption, it must be possible to safely and economically transport hydrogen gas to users. One possible method for conveniently transporting hydrogen would be to use the existing underground natural gas pipeline network. Successful use of this distribution system, however, depends on its compatibility with hydrogen gas.

The natural gas distribution network consists primarily of carbon-manganese steel pipe sections with diameters up to 48 inches. Except for seamless pipe that is available only with diameters less than about 24 inches, all pipe sections have a longitudinal or spiral seam weld. The pipe sections are joined in the field with manual girth welds before laying in the ground. For external corrosion protection, pipe sections are coated with various organic coatings (e.g. coal tar, asphalt, epoxy, polyethylene) and cathodically protected. Typical pipeline operating pressures with natural gas generally do not exceed 1000 psi (6.9 MPa). For long-distance transport, the gas pressure is maintained by periodically spaced in-line compressors.

The major concern with use of the natural gas pipeline network to transport hydrogen is due to the possible embrittlement of the line-pipe steel, weldments, and compressors by hydrogen gas. Practically all metallic materials exhibit degradation of their mechanical properties when tested in gaseous hydrogen. The severity of this degradation depends on many variables including the alloy composition, its yield strength, hydrogen pressure, hydrogen purity, temperature, type of test performed (e.g. tensile test or crack-growth test), and rate of load application. The carbon and alloy steels that constitute the gas pipeline system unfortunately are one of the generic groups of materials most highly susceptible to gaseous hydrogen embrittlement.

HYDROGEN EMBRITTLEMENT OF STEELS

Although the mechanistic details of hydrogen embrittlement are still a subject of considerable research (Reference 1), the influence of the important variables that control the degree of hydrogen degradation of various mechanical properties are well-known. First of all, for hydrogen gas to embrittle ferritic steels at temperatures less than 200 C, the steel must be deformed or tested in the presence of hydrogen gas. Temporary exposure to hydrogen gas below 200 C, even at very high pressures, does not permanently degrade the steel. Hydrogen gas and deformation must both be present.

Mechanical properties that are affected by exposure to hydrogen include tensile ductility, notch strength, fracture toughness, smooth and notched-bar fatigue life, and fatigue-crack-growth resistance. Two additional phenomena that are observed in hydrogen are subcritical-slow-crack growth and surface crack initiation on smooth bars. The severity of these effects depend primarily on the yield strength of the steel (governed by composition, heat treatment, and prior deformation), hydrogen pressure, hydrogen purity, temperature, and rate of loading.

The most important variable controlling hydrogen degradation is the yield strength. Even though hydrogen degrades properties of very low yield strength steels, the severity of property loss, especially for those properties that are important for structural integrity, increases with increasing yield strength. Alloy composition does not appear to be extremely important, and hydrogen compatibility can be roughly ranked by yield strength. Table 1 lists observed property loss by yield strength.

Hydrogen degradation of a given steel increases with increasing hydrogen pressure and hydrogen purity and decreases with increasing loading rate. Temperature dependence is not monotonic. Maximum susceptibility to hydrogen embrittlement occurs at temperatures between -100 C and 20 C (Reference 2). The hydrogen pressure dependence of embrittlement is not strong, usually increasing as the square-root of hydrogen pressure (Reference 3). Degradation is extremely dependent on certain impurities in the

TABLE 1. REPORTED PROPERTY LOSSES IN STEELS EXPOSED TO GASEOUS HYDROGEN

	Yield Strength			
Property	Up to 400 MPa	400-600 MPa	600-1000 MPa	>1000 MPa
Tensile Properties				
Loss of ductility	Yes	Yes	Yes	Yes
Loss of notched-strength	Yes	Yes	Yes	Yes
Surface cracking	Yes	Yes	Yes	No(1)
Delayed failure	No	No	Yes	Yes
Fatigue Properties				
Loss of fatigue life(2)	Yes	Yes	Yes	Yes
Fracture Properties				
Decreased fracture toughness	Yes(3)	Yes(3)	Yes	Yes
Subcritical-crack growth	No	No	Yes	Yes
Increased fatigue-crack growth rate	Yes	Yes	Yes	Yes

(1) Numerous surface cracks are not observed because the first crack formed leads to failure.

(2) Fatigue life includes the times for initiation and growth of cracks. Cyclic loading well below yield does not lead to fatigue life losses. Increasing loss of fatigue life is observed for cyclic loading that produces increasing amounts of yielding.

(3) Subcritical-crack growth is not observed in lower strength steels. Losses in fracture toughness due to hydrogen have been determined using elastic-plastic fracture mechanics techniques.

hydrogen gas. Small additions of oxygen, carbon monoxide, or water vapor have been shown to inhibit much of the damaging effects of hydrogen (Reference 4). Hydrogen degradation has been found to increase with decreasing loading rates in tensile studies (Reference 5), fracture studies (Reference 6), and fatigue studies (Reference 7).

INTEGRITY OF PIPELINES TRANSPORTING HYDROGEN

To date, the great majority of pipeline failures have been the result of events occurring on the outside of the pipe. With the prospects of transporting hydrogen or hydrogen/synthetic natural gas mixtures through pipelines, new problems could arise with possible degradation occurring from the inside of pipelines. Both short-term and long-term compatibility of pipelines and compressors with hydrogen must be assured before routine transport of hydrogen can become a reality.

Since pipelines and compressors are designed to operate with nominal stresses significantly below yield, chances of pipeline failures related to hydrogen-induced loss in ductility or loss in smooth-bar fatigue life probably are remote. However, the influence of hydrogen at internal stress raisers such as weld cracks could present significant problems. Since typical line-pipe base metals have yield strengths below that where static-load subcritical-crack growth is observed in hydrogen, the primary degradation problem in base metal is likely to be hydrogen-enhanced fatigue-crack growth. Gas transmission pipelines are designed to operate as statically-loaded structures, and to the authors' knowledge, no pipeline failures have occurred by fatigue during transport of natural gas. However, some fatigue loading of a pipeline is unavoidable due to minor operating pressure variations and occasional shut-downs. Fatigue-crack growth has been observed to be accelerated by an order of magnitude in 1000 psi (6.9 MPa) hydrogen in steels similar to line-pipe grades (Reference 7). Moreover, researchers at Sandia National Laboratories (Reference 8) have reported through-wall fatigue-crack growth of a pipe section starting from a quarter-wall-penetration defect on the fifth hydrogen pressurization cycle to 1000 psi (6.9 MPa).

A second potential hydrogen compatibility problem exists in pipeline welds. Sandia researchers have reported sustained-load subcritical-crack growth near heat-affected zones of line-pipe steel welds in 1000 psi (6.9 MPa) hydrogen gas.

No information exists on the use of in-line compressors with hydrogen. By design, however, they are continually subjected to fatigue loading. Their compatibility could be limited by the presence of any pre-existing flows on metal parts exposed to hydrogen.

Problems with fatigue-crack growth and subcritical-crack growth could eliminate the possibility of transporting pure hydrogen through underground steel pipelines or require such stringent operating conditions and quality-control standards that hydrogen transport would be impractical. One reassuring prospect, however, is that small amounts of several other additive gases could inhibit the hydrogen degradation altogether. Ethane, ethylene (both, Reference 9), acetylene (Reference 10) as well as oxygen, carbon monoxide, and water vapor (all, Reference 4) show promise in this regard.

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PROJECT SUMMARY

Project Title:	Development of a Metal Hydride Process for Hydrogen Recovery
Principal Investigator:	Dr. E.L. Huston
Organization:	Ergenics Division MPD Technology Corporation 681 Lawlins Road Wyckoff, NJ 07481 (201) 891-9103 Note: Air Products and Chemicals, Inc. and INCO Research and Development Center, Inc. are subcontractors.
Project Goals:	The primary objective of this project is the development and demonstration of a process for recovering hydrogen from waste gas streams based on metal hydride technology. The waste gas streams exist in chemical plants and refineries with a total hydrogen content of $3X10^9$ SCF/D and a potential resource recovery of 0.1 Quad.
Project Status:	Phase I - Process Identification is scheduled for completion 10/31/81. Waste gas streams have been surveyed and candidates identified. Hydride-impurity interactions have been studied as a function of metal hydride former ($LaNi_5$, $(FeMn)Ti$, $(FeNi)Ti$, $La(NiAl)_5$, Mg_2Ni and Mg_2Cu), reaction temperature (0-350°C), impurity species and impurity concentration. Waste-gas pretreatment processes and cost impacts have been determined for removal of specific poisons. Seven topical reports have been delivered. Process Integration and economic evaluations are in progress. A go/no go decision will be made at the end of Phase I regarding the design (PhaseII), construction and operation (Phase III) of a Pilot Demonstration Unit.
Contract No.:	BNL-509926-S
Contract Period:	August 14, 1980 - October 31, 1981
Funding Level:	Phase I - $337,327 Subsequent Phases total about $900,000 For a three-year program total of $1,200,000.
Funding Source:	DOE CHEMICAL/HYDROGEN ENERGY STORAGE SYSTEMS Cost Sharing 14.75% or $58,400 additional for Phase I.

BEST DOCUMENT AVAILABLE

METAL HYDRIDE PROCESS FOR HYDROGEN RECOVERY

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201-891-9103

ABSTRACT

A metal hydride process for the recovery of hydrogen from industrial waste-gas streams ($1-10\times10^6$ SCF/D) is being developed. Waste gas streams have been surveyed and candidates identified. Hydride-impurity interactions have been studied as a function of metal hydride former ($LaNi_5$, (FeMn)Ti, (FeNi)Ti, $La(NiAl)_5$, Mg_2Ni and Mg_2Cu), reaction temperature (0-350°C) impurity species and impurity concentration. Waste-gas pretreatment processes and cost impacts have been determined for removal of specific poisons. These results have been used as the basis for an initial process design and cost estimate.

INTRODUCTION

The chemical and refining industries currently generate more than 32×10^9 SCF of hydrogen daily. The annual energy equivalent of this hydrogen is 3.5 Quads. Most of this hydrogen is produced by steam reformation of natural gas or other premium feedstocks. Hydrogen consumption within these industries is estimated at 80-90% of production. The balance of the hydrogen is delivered to waste-gas streams for process fuel or disposal by flaring or venting. These streams are often low in pressure and highly diluted with impurities (<60% hydrogen) so that further hydrogen recovery by conventional cryogenic or pressure swing adsorption (PSA) is not economic.

Development of a new process for hydrogen recovery from low pressure, low hydrogen streams would establish a large (3×10^9 SCF/D) geographically distributed source of secondary hydrogen. Incentives for recovery of this hydrogen are based on at least three factors: the differential between the chemical and fuel value, established markets for secondary hydrogen and conservation of non-renewable natural resources.

A separation process based on the absorption of hydrogen by reversible metal hydrides has been demonstrated on a bench scale (1,2). A brief description of the process was given earlier (3) and a more detailed discussion with additional bench scale tests are given in (4). Advantageous features of a hydride-dehydride separation/recovery process include:

1. Reaction Specificity - Only hydrogen reacts, process useful for dilute streams
2. High Recovery - Determined by hydrogen pressure and hydride plateau pressure.
3. Rapid kinetics of hydrogen reactions.

This contract represents Phase I of a three phase (three year) program for the development and demonstration of a metal hydride based hydrogen recovery process applicable to industrial scale (1-10X10^6 SCF/D) waste gas streams. Phase I addresses waste stream and site selection, stream pretreatments, hydride-impurity gas interactions (poisoning and regeneration) process integration and economic evaluation. Phase I runs for 15 months, ending Oct. 31, 1981. Assisting ERGENICS as subcontractors are Air Products and Chemicals, Inc. and INCO Research and Development Center, Inc. As of this writing, seven topical reports have been delivered describing both analytic and exprimental work on various aspects of the program.

OFF-GAS STREAM SURVEY

Over forty sources of off-gas (secondary) hydrogen are found in the chemical and petroleum refining industries. Table I gives the larger sources in terms of the number of sites and total (potentially available) volume of off-gas hydrogen. this analysis accounts for 2.1X10^9 SCF/D of hydrogen or about two-thirds of the expected total. An additional .5X10^9 SCF/D of hydrogen in the petroleum industry was excluded from Table I because the stream chemistries are suitable for re-reformation.

Table I - Summary of Hydrogen Off-Gas Streams in US Chemical and Petroleum Industries.

Industry	No of Sites	Total H_2 available (10^6 SCF/D)	% of Total	P/C Key
Acetylene	6	110	5.2	J
Ammonia	99	247	11.8	-
Butadiene	11	120	5.7	H
Chlorine	60	334	15.9	P
Formaldehyde	34	34	1.7	G
Methanol	12	106	5.1	K
Olefins	36	756	36.1	B,C,F
Pet.Refining	350	300	14.3	A,D,E
Styrene	13	89	4.2	L
	Total	2096	100.0	

The off-gas streams identified in Table I are plotted on an Applications Map, Fig. 1, according to the total stream pressure and hydrogen content. This map is divided into regions where the various hydrogen separation technologies will likely have a competetive (economic) advantage. The shaded boundries represent overlaps (competetion) between technologies. Development of this map requires a great many simplifying assumptions. The boundaries are sensitive to stream size, impurity type and product hydrogen purity, % recovery and pressure. In spite of these assumptions, the map is valuable in selecting those streams for consideration for hydride separation.

Streams A,B,D and H were selected for the initial evaluation. In addition to hydrogen, these streams contain CH_4, CO_2, H_2O, NH_3, H_2S and C_2 to C_7's the amount of CO is generally low although precise levels are not available.

The Ammonia Purge Gas stream has been obmitted from this program. This stream is essentially inert to metal hydrides (4) and a pilot separation plant (5000 SCF/D) has been built independently by APCI, INCO and MPD. Pilot plant results and expierence will be utilized in Phases II and III of this program.

HYDRIDE-IMPURITY INTERACTIONS

The off-gas streams of interest contain many components in addition to hydrogen Qualitative (screening) and quantitative determinations of the effects of single impurity species on hydrogen absorption and desorption by the hydride formers has been the major experimental effort in this program. For a given process gas stream, it is hoped that an alloy can be specified with no deleterious gas impurity interactions. If this is not feasible, then the impurity must be either removed by pretreatment or the alloy shown to respond to simple regeneration treatments.

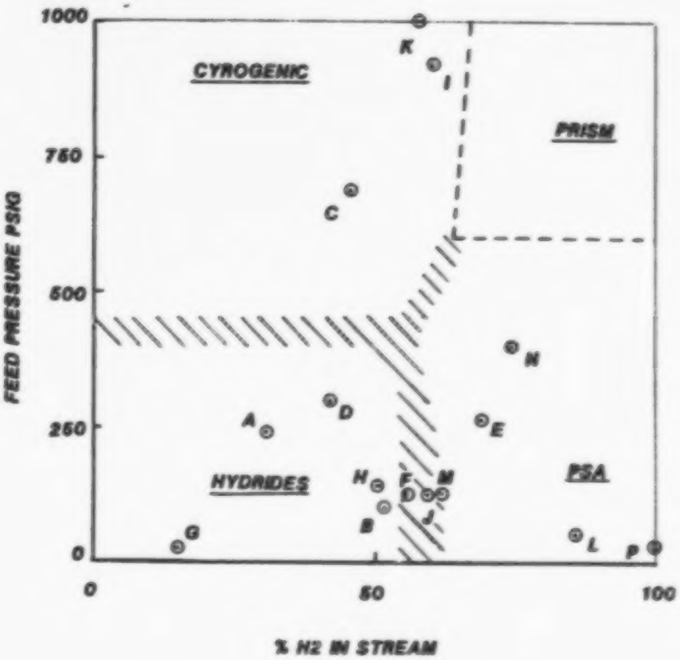

Figure 1 Applications Map for the Recovery of Hydrogen from Industrial Off-Gas Streams.

Screening tests were done by measuring the hydrogen absorbed during exposure, for a fixed time, of a previously activated sample to a binary gas mixture under controlled conditions of temperature pressure and composition. The effect of an impurity was judged from the absorption response during successive cycles (usually 10-40). A summary of the screening tests is given in Table II. Designations by primary effect are:

I= Inert, H= Inhibits Absorption Kinetics
C= Capacity Gradually Reduced, P= Poision by Surface Occlusion

Designations enclosed in brackets were obtained from low pressure impurity adsorption tests. The reader is cautioned that this table is intended only as a ROUGH QUALITATIVE GUIDE to impurity interactions. Detailed information about each test is avaiable in the Topical Reports.

CO poisoning, previously thought to be the Achilles' heel of reversible metal hydrides, is dramatically lessened by selecting operating temperatures above 100°C. In this regime, CO is methanated and operation with CO concentrations in excess of .1% have been demonstrated. Oxygen tolerance, on the other hand, is generally improved by lowering temperature. The addition of Al to $LaNi_5$ and Ni to FeTi has also been shown to be beneficial. Sulfur containing impurities, H_2S and COS, have been found to be poisons at both low and intermediate temperatures. The impurity tolerance of Mg-base hydride formers is being systematically examined for the first time in this program.

More detailed interaction studies have led to the formulation of a predictive model for the damage caused by impurities. The model is applicable for two mechanisms: surface site blockage and bulk phase consumption. Additional studies have examined the combined effects of $CO + O_2$ on $LaNi_5$, regeneration effectiveness, and hydride former pretreatments. Hydrogen break-thru has been characterized for $LaNi_4Al$ and work is underway with Mg_2Ni to provide preliminary design information for separator columns.

Table II Summary of Screening Tests for Alloy-Impurity Interactions

Alloy	TEMP (°C)	CO	O_2	H_2O	CO_2	H_2S	NH_3	N_2	CH_4	C_2H_4	MOH	COS	Amine
					Impurity Concentrations ∿1 to 3%								
Mg Ni	300	I-H	-	I	H-C	I-H	P	-	H	H	H	P	-
$LaNi_4Al$	150	H	-	-	I	P	I	-	-	-	-	-	-
	115	H	-	-	-	-	-	-	-	-	-	-	-
					Impurity Concentrations ∿0.1%								
$LaNi_5$	115	H-C	C	-	-	-		-	-	-	-	-	-
	85	P	C	-	H		I-H	I	I	I	-	-	-
	25	P	C	I-H	H	(P-C)	(I-H)	-	(I)	(I)	(H)	-	(I)
(Fe,Mn)Ti	115	H	-	-	-	-	-	-	-	-	-	-	-
	85	P	H-C	-	H	-	-	-	-	-	-	-	-
	25	P	P	P	-	(P-C)	-	-	(I)	(I)	(H)	-	(I)
$LaNi_{4.7}Al_{.3}$	115	H-C	H-C	-	-	-	-	-	-	-	-	-	-
	85	P	H-C	-	-	-	-	-	-	-	-	-	-
	25	P	H	-	-	-	-	-	-	-	-	-	-
(Fe,Ni)Ti	115	H	-	-	-	-	-	-	-	-	-	-	-
	85	P	H-C	-	-	-	-	-	-	-	-	-	-
	25	P	H	-	-	-	-	-	-	-	-	-	-
FeTi	115	H	-	-	-	-	-	-	-	-	-	-	-
	85	P	H-C	-	-	-	-	-	-	-	-	-	-
	25	P	P	P	-	-	-	-	-	-	-	-	-

GAS PRETREATMENTS

An Alternative approach to management of alloy-impurity gas interactions is to remove (reduce) known poisons in the process stream prior to contacting the hydride beds. Pretreatment options have been identified from the literature. Preliminary capital and operating costs were generated for cases in which a single gaseous impurity is to be removed (reduced). The impurities examined include CO, CO_2, H_2S, H_2O, RSH and COS.

Table III Summary of Off-Gas Stream Pretreatment Costs.

Impurity	Feed Concentration (Vol %)	Process Option	Impurity In Product (%)	Typical Costs ($/MSCF Feed)
CO	0-2	$M^{(a)}$	0.001	0.05 - 0.15
CO_2	2-10	$A^{(b)}$	0.10	0.05 - 0.20
H_2S	0.01-1.0	A	0.001	0.05 - 0.25
H_2O	0.1 - 0.25	A	0.01	0.03 - 0.075
RSH	0.01-0.5	A	0.001	0.10 - 0.30
COS or CS_2	0.01-0.5	$C^{(c)}$-A	0.001	0.075 - 0.175

(a) Methanation, $CO+3H_2 \rightleftarrows CH_4+H_2O$

(b) Adsorption on molecular sieve

(c) Catalytic conversion to H_2S.

The following typical stream was considered to be the base case: i) pressure, 250 psig; ii) H concentration, 50%; iii) temperature, 77°F; iv) flow rate, 2-12X10^6 SCFD; and v) a single impurity. Due to the relatively small stream size, physical adsorption (i.e, PSA) is the preferred economic process option, over chemical absorption(i.e., solvent extraction).

Table III summarizes the pretreatment options and costs for the cases considered. For the most part, the costs are in the range $0.05-0.25/1,000 SCF feed, with H O removal being less than $0.1/1,000 SCF feed. Associated with these cost figures is a ±30% uncertainty. Relative to the costs shown in Table III, increasing the pressure and hydrogen concentration of the stream will lower the costs. The converse is true. The pretreatment costs will increase if lower impurity levels are required in the product stream. Multiple component effects have not been considered at this stage.

SEPARATION COSTS

Preliminary separation costs have been estimated for a case similar to D of Fig.1, the purge gas from a petroleum refinery hydroprocessing unit. The costs are based on a plant design consisting of 3 hydride beds in parallel to provide continuous hydrogen production. An alloy system capable of operating at low to intermediate temperatures (such as $LaNi_{5-x}Al_x$) was selected. Feed conditions were: 300 psig total pressure, 43 mole% hydrogen, variable flow rate, no impurities requiring gas pretreatment. Costs were calculated as a function of hydrogen production (1-5X10^{6}SCF/D) for a product stream at 200 psig and 95% purity. Hydrogen recovery was set at 85%.

A summary of capital and operating costs are given in Fig 2. At a recovery rate of 5X10^6 SCF/D, the installed cost is estimated to be approximately $3X10^6. Fifty to sixty percent of this figure is hydride materials. Operating costs of about \$2/MSCF H_2 are insensitive to the production rate over the range 1-5X10^6 SCF/D. Operating costs include a \$.85/MSCF H_2 component which represents the fuel value of the hydrogen removed from the feed stream. Operating costs in Fig 2 were calculated assuming no alloy replacement. Annual replacement of the bed with no credit for salvage would add approximately \$.95/MSCF H_2.

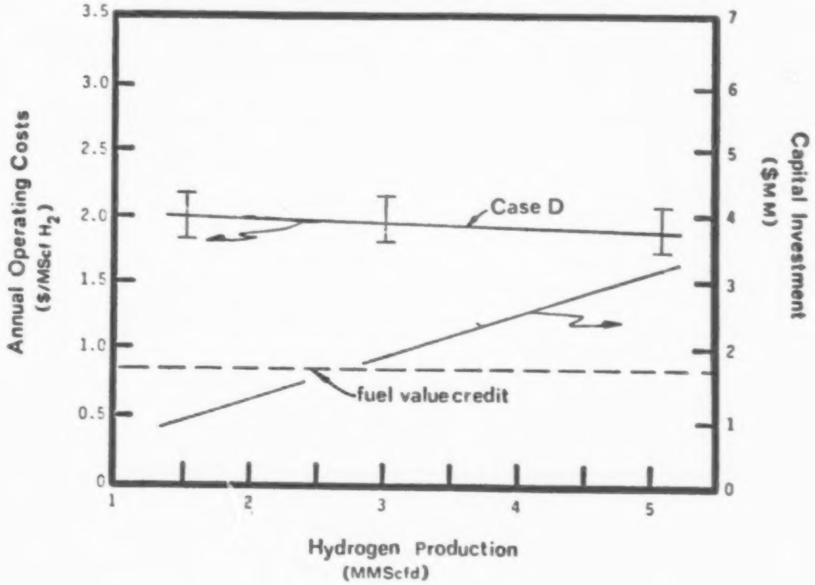

Figure 2 Hydrogen Separation Cost Summary

Feed: 300 psig (total)
43% hydrogen
No pretreatment

Product: 200 psig (total)
95% hydrogen
85% recovery

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Hydrogen produced in 1981 by steam reformation of natural gas ($3/10^6 BTU) costs approximately $2.20 to $3.50/MSCF H_2 for quantities exceeding 5X10^6 SCF/D. Separation cost estimates obtained in this study are comparable when the fuel value credit is included. The Natural Gas Policy Act of 1978 mandates natural gas prices to rise to $6/10^6 BTU by 1985. Based on natural gas pricing alone, separation costs are expected to rise at only 1/3 the rate of production costs. Thus deregulation will favor increased hydrogen recovery.

CONCLUSIONS

A survey of off-gas streams in the chemical and petroleum refining industries have identified 2.1X10^9 SCF/D of hydrogen potentially available for recovery. Alloy-impurity interactions have been extensively studied. A wide range of operating conditions were identified with little or no poisoning by specific impurities. Sulfur containing gases will probably require stream pretreatment. Cost studies show the recovery of hydrogen from a 42%, 300 psig off-gas stream to be cost competetive today with the production of additional hydrogen by steam reformation of natural gas. Future natural gas cost escallations will favor recovery.

FUTURE WORK

In the remaining two months of Phase I, five topical reports will be completed and the Final Report written and delivered. The favorable cost studies obtained in this program to date require further experimental verification. Hence the recommendations for the Phase II program will include the generation of engineering data on the bench-scale separation of a multi-component pretreated stream. These data will then be used to design a Process Demonstration Unit and refine the separation cost estimates.

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2) V. Cholera and D. Gidaspow, "Hydrogen Separation and Production from Coal Derived Gases Using Fe_x $TiNi_{1-x}$" Proc. 12th IECEC, 1976 Stateline, NV, I, 981.

3) E.L. Huston, "Development Status of a Metal Hydride Process for Hydrogen Recovery", Proc. DOE Thermal and Chemical Storage Annual Contractor's Review Meeting (801055), Oct. 1980, McLean, VA, 170.

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PROJECT SUMMARY

Project Title: Hydrogen Recovery from Hydrogen Sulfide

Principal Investigator: D. L. Hildenbrand

Project Leader: G. N. Krishnan

Organization: SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Project Goals: Perform bench scale experiments to obtain kinetics of reaction of hydrogen sulfide with liquid copper for the purpose of converting hydrogen sulfide to hydrogen.

Project Status: A 3.6 cm i.d. bench reactor has been constructed. Preliminary experiments have shown that the reaction of hydrogen sulfide with liquid copper at 1200°C is rapid. The conversion of hydrogen sulfide to hydrogen was found to be in excess of 99% when the gas residence time is greater than a few hundred milliseconds. A larger, 10 cm i.d. reactor is under construction to study the reaction kinetics at flow rates higher than 1 standard liter per minute.

Contract Number: 532360-S

Contract Period: January 15, 1981 through January 14, 1982

Funding Level: $105,651

Funding Source: Brookhaven National Laboratory

RECOVERY OF HYDROGEN FROM HYDROGEN SULFIDE

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ABSTRACT

A process to recover hydrogen from hydrogen sulfide was developed and in which hydrogen sulfide reacts with liquid copper to form cuprous sulfide and hydrogen. In a subsequent step the copper is recovered by oxidizing the sulfide. Preliminary bench scale experiments have shown that the reactions are rapid and approach equilibrium conversions with a gas residence time of a few hundred milliseconds.

INTRODUCTION

Increasingly large amounts of hydrogen sufide are currently being generated from the desulfurization of sour crude oil and sour natural gas deposits. Current annual production of hydrogen sulfide is about 10 million tons and this is expected to double by the year 2000. Currently hydrogen sulfide is being converted by the Claus process into sulfur for storage or for production of sulfuric acid. However during this conversion, the hydrogen component of hydrogen sulfide is lost as water. It is highly desirable to recover this hydrogen and it is estimated that 7.7×10^9 cubic meters per year of hydrogen can be produced from hydrogen sulfide.

The direct thermal decomposition of hydrogen sulfide to hydrogen and sulfur is strongly endothermic and the equilibrium yield is rather low (< 2%) below 800°C. Many metals can react with hydrogen sulfide to produce hydrogen and a metal sulfide. However only a few metal sulfides such as sulfides of lead, silver, mercury, arsenic, bismuth, copper and nickel can be oxidized to the corresponding metals instead of metal oxides at reasonable temperatures. This property is essential in order to recycle the metal for reaction with hydrogen sulfide. Based on factors such as metal availability, low price, nontoxicity, and OSHA standards copper outranks the other candidates. Both copper and cuprous sulfide are liquids above 1125°C and are immiscible. Above that temperature both sulfidation and oxidation are gas-liquid reactions and the rates are expected to be high.

Based on the above factors, in 1978, SRI invented a process[1] in which hydrogen sulfide is bubbled through liquid copper to produce hydrogen and cuprous sulfide. In a subsequent step the cuprous sulfide is oxidized with air to recover copper and produce sulfur dioxide which can then be converted to sulfuric acid. Thus in this SRI process there is no net consumption of copper. The copper recovery step is identical to the "white metal blowing" step in commercial production of copper and thus a large technology base exists for the SRI process.

The thermodynamics of Cu-S system is well known. Both the sulfidation and oxidation are thermodynamically favorable and are exothermic at the typical operating temperature of 1200°C.

$$2Cu(\ell) + H_2S(g) \rightarrow Cu_2S(\ell) + H_2(g) \qquad (1)$$

$$\Delta H^0_r\ (1500\ K) = -11.6\ kcal.mole^{-1}$$

$$\Delta G^0_r\ (1500\ K) = -17.0\ kcal.mole^{-1};\ K = 306$$

$$Cu_2S(\ell) + 4.76\ air(g) \rightarrow 2Cu(\ell) + SO_2(g) + 3.76\ N_2(g) \qquad (2)$$

$$\Delta H^0_r(1500\ K) = -53.1\ kcal.mole^{-1}$$

$$\Delta G^0_r(1500\ K) = -39.2\ kcal.mole^{-1};\ K = 5.4 \times 10^5$$

Including the sensible heat for preheating the reactant gases the sulfidation reaction is slightly endothermic (0.9 kcal.mole^{-1}) and the oxidation reaction is highly exothermic (-8.9 kcal.mole^{-1}). The product gases exit the reactor at high temperature and they can be used for preheating the reactant gases and to produce process steam. The equilibrium conversion of hydrogen sulfide to hydrogen at 1500 K is estimated to be 99.7%. Under equilibrium conditons the residual oxygen concentration during the oxidation step is a only a fraction of one part per million.

Because of commercial practice the oxidation of cuprous sulfide has been well studied. However very little was known about the kinetics of reaction of hydrogen sufldie with liquid copper. Thus the object of the current program at SRI is to study under bench scale conditions the kinetics of the reaction of hydrogen sulfide with liquid copper for the purpose of producing hydrogen.

EXPERIMENTAL RATE MEASUREMENTS

Apparatus. A schematic diagram of the apparatus assembled for the preliminary rate measurements is shown in Figure 1. The apparatus consists of an alumina reactor of 4.4 cm i.d. heated by an 1500^{0}C electrical resistance heating muffle furnace. The furnace can be heated to 1500^{0}C and can maintain a constant tdmperature zone of 10 cm at 1200^{0}C. The copper melt contained in an alumina crucible inside the reactor. Hydrogen sulfide is metered through a mass flow meter and is introduced into the copper melt by means of alumina, quartz or mullite nozzles. The product gases exit the reactor near the top and are analyzed for hydrogen, hydrogen sulfide and other gaseous reaction products by gas chromatography. Two gas chromatographs are used in parallel, one for measurement of hydrogen and the other for measurement of hydrogen sulfide and other gases. Provisions are made for evacuating the reactor, for purging with an inert gas and for introducing gaseous impurities such as methane or carbon dioxide. The hydrogen sulfide stream can be replaced with oxygen or air for the purpose of oxidizing cuprous sulfide back to copper. A Pt, Pt-10% Rh thermocouple is used to measure the temperature of the melt. OFHC copper and technical grade gases were used as reactants.

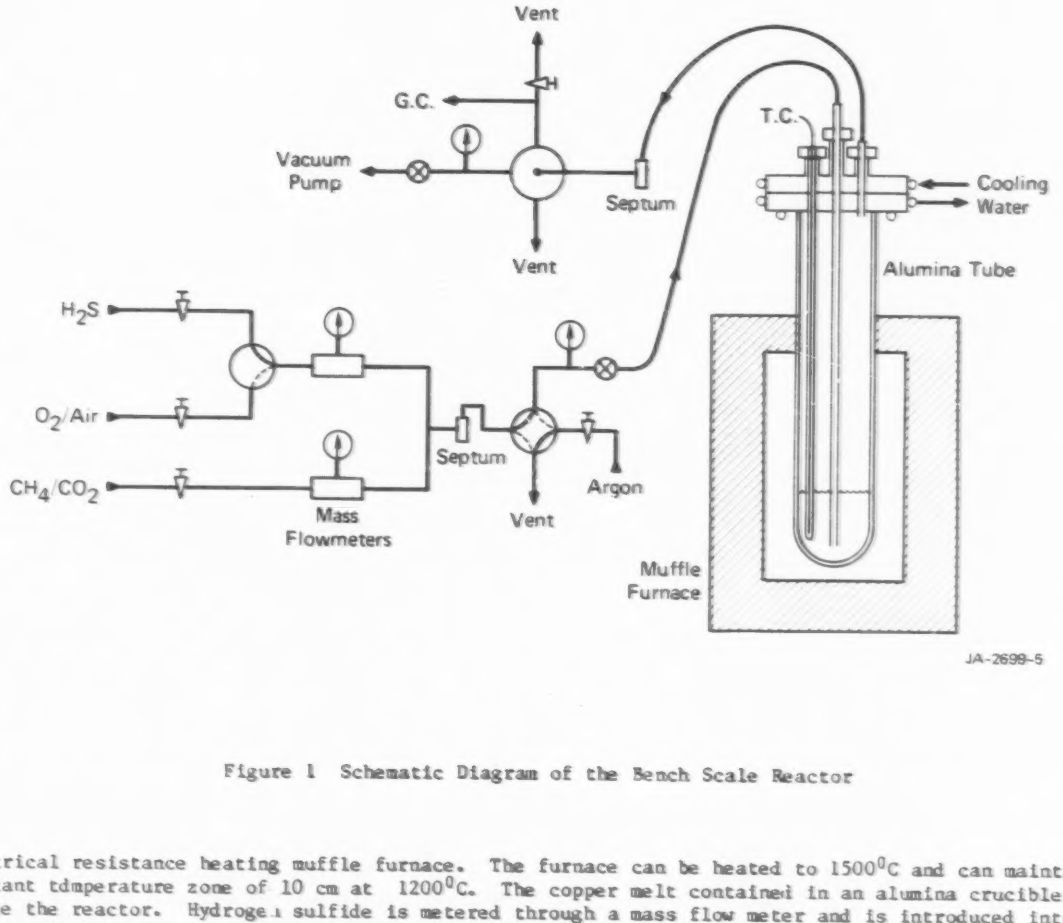

Figure 1 Schematic Diagram of the Bench Scale Reactor

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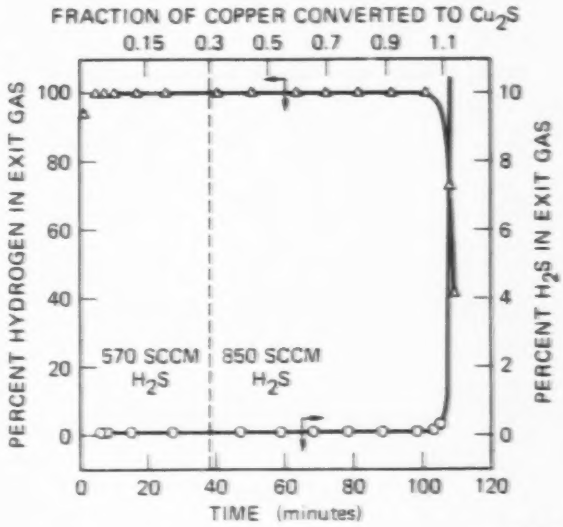
Experimental Results At 1200^0C the rate of reaction of hydrogen sulfide with liquid copper was rapid and the conversion to hydrogen was found to be near the equilibrium level. Figure 2 illustrates the composition of reactor exit gas as a function of time when hydrogen sulfide was used as the reactant gas. The calculated conversion of copper to cuprous sulfide is also shown.
It is seen that the rate of reaction remains constant until nearly all the copper is converted into cuprous sulfide. This is because (1) copper and cuprous sulfide are immiscible liquids at the reaction temperature, (2) cuprous sulfide is less dense than copper and (3) the reaction rate is rapid. The immiscibility and the difference in density assures the movement of cuprous sulfide product away from the reaction interface leaving fresh copper for further reaction. Because of the rapid reaction rate the residence time of the gas can be relatively short.



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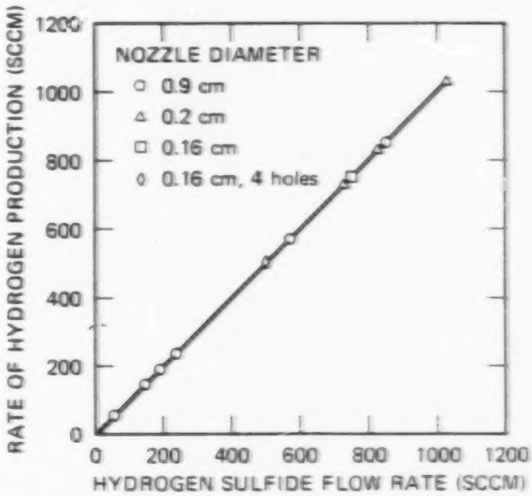

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Figure 2. Composition of reactor exit gas as a function of reaction time; initial melt height = 3.5 cm, nozzle diameter = 0.9 cm.

Figure 3. Rate of production of hydrogen as a function of hydrogen sulfide flow rate.

Figure 3 illustrates the rate of production of hydrogen as a function of hydrogen sulfide flow rate and injection nozzle diameter. At high flow rates violent splashing of the melt and excessive vibration of the lance occurred thereby limiting the flow rate to 1000 SCCM in the present reactor. The rate of hydrogen production did not change with the increasing flow rate under the conditions studied. Even at the highest flow rate used the rate of hydrogen sulfide conversion remained at 99.9% until nearly all the copper was converted to cuprous sulfide. It is estimated that a gas residence time in the order of a few hundred milliseconds is sufficient for the completion of reaction.

A few experiments concerning the oxidation of cuprous sulfide were also carried out. This reaction step has been well studied and is practiced commercially. Under our laboratory conditions copper sulfide can be converted to copper using air or oxygen. At high flow rates of oxygen some copper oxide was formed near the lance tip and apparently reacted with the alumina. Use of a magnesia tube, a lower flow rate of oxygen, or use of air should alleviate this problem.

Carbon dioxide and hydrocarbons such as methane are potential impurities in hydrogen sulfide streams. Hence hydrogen sulfide containing 10% CH_4 or 10% CO_2 was allowed to react with liquid copper at 1200^0C. The presence of these impurities did not affect the hydrogen sulfide conversion rate. Methane decomposed to produce hydrogen and a carbon deposit inside the reactor. Carbon dioxide was transformed into carbon monoxide by reverse water gas shift reaction as follows

$$2Cu + H_2S \rightarrow Cu_2S + H_2 \tag{3}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{4}$$

Process Flow Sheet Development

Since petroleum refineries processing sour crude oil are a major source of hydrogen sulfide and also a major consumer of hydrogen, it would be appropriate to situate the hydrogen recovery reactor near a petroleum refinery. A study is underway to develop a flowsheet for processing 265 tons of hydrogen sulfide per day. There are several petroleum refineries in the United States that produce this or a higher amount of hydrogen sulfide. The results of the process flow sheet study will be available shortly. The hydrogen recovery process can also find application near sour natural gas wells. The hydrogen produced can be piped along with the natural gas or converted to ammonia or ammonium sulfate for shipping.

FUTURE WORK

A larger, 10 cm diameter reactor is currently under construction and this reactor will be used to introduce H_2S up to a maximum flow rate of 10 std liters per minute. By varying the depth to which the gas is introduced and by monitoring the conversion of H_2S to H_2, the reaction rates constant will be evaluated. Effect of temperature, gas velocity, impurities in the gas stream, and injection nozzle size on the reaction rate will be studied. The sulfided copper will be regenerated using oxygen or air. A mathematical model describig the reaction kinetics will be developed using the experimental results.

CONCLUSIONS

Preliminary studies have shown that the reaction of hydrogen sulfide with liquid copper is rapid and the conversion of hydrogen sulfide to hydrogen is nearly complete when the residence time is greater than a few hundred milliseconds.

REFERENCES

1. R. W. Bartlet, et al., Preliminary Evaluation of Processes for Recovering Hydrogen from Hydrogen Sulfide. Final Report to JPL under contract No. 955272. SRI International, July 1979.

PROJECT SUMMARY

Project Title: Systems Analysis of Hydrogen/Natural Gas Supplementation and Separation

Principal Investigator: Morris Beller

Organization: National Center for Analysis of Energy Systems
Brookhaven National Laboratory
Upton, New York 11973

Project Goals: Identify the barriers and incentives associated with the long-range application of hydrogen gas supplementation in the natural gas system. Explore the additional option of separating the hydrogen from the mixed stream for industrial use. Use a specific region to perform the analysis in terms of current and new markets for hydrogen. Perform a brief estimate of economic factors.

Project Status: A candidate region for analysis was selected based upon a set of prescribed criteria. A baseline set of energy supplies and demands for the region was developed to assess the total present and possible future place for hydrogen in the system. A market study was conducted to evaluate present hydrogen use and future industry implications. A workshop was conducted to assess the perceptions of industries and utilities regarding the supplementation and separation concept, and to outline the barriers and incentives arising from such perceptions. A 1977 Ad Hoc Committee Report on the hydrogen supplementation study was assessed on the basis of workshop results and todays understanding of the U.S. energy situation. The economic analysis was completed. The final report is in preparation.

Contract Number: DE-AC02-76CH00016

Contract Period: October 1, 1980 - September 30, 1981

Funding Level: $120,000

Funding Source: U.S. Department of Energy

SYSTEMS ANALYSIS OF H_2/NATURAL GAS SUPPLEMENTATION AND SEPARATION

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ABSTRACT

A systems analysis of the concept of supplementing natural gas with hydrogen was conducted in terms of present fuel supplies and prices. An added option was analyzed; this involves separation of the hydrogen from the mixed stream for use as a nonenergy commodity. The study concludes that no insurmountable barriers exist for the supplementation concept; the separation option will depend only upon economic factors.

INTRODUCTION

An Ad Hoc Committee investigated the concept of hydrogen supplementation of natural gas in June 1977, concluding[1] that the concept had little merit in the mid-term (1985-2000) for commercialization, but that R&D efforts should continue. The likely hydrogen supply assumed by the Committee was electrolytic hydrogen from off-peak and/or spinning reserve electric generating capacity although SNG production by coal gasification, the use of renewable resources and installed electric generating capacity were also considerated as possible sources of hydrogen. Considering the current economic and energy supply situation in the U.S. regarding natural gas and other energy resources in comparison to the situation at the time of the Committee's work, a thorough review of the Committee's assumptions and their findings is in order. Currently, there is a deregulatory mood in the political arena which has already deregulated the crude oil price and may also deregulate the price of natural gas by 1985 or before. Moreover, official projections of the supply of natural gas in the mid-term as well as the long-term future are considerably more pessimistic than those made only five years ago. In addition, the supplementation concept can now offer an added option, hydrogen separation for industrial usage, which was not considered by the Committee.

METHODOLOGY

The methodology for the study involved first selecting a specific site for the study, since using national estimates tends to obscure specific regional issues and problems which are critical to the evaluation of such concepts. After the selection of the site, the evaluation focused upon specific potential markets for hydrogen, and then examines the mix of customers comprising these markets. A workshop at this point of the study helped to establish an appropriate set of barriers and incentives for the concept. Finally, an economic analysis was performed to assess the existence of a time-envelope for market penetration.

SITE SELECTION

The site selection criteria for the study were relatively straight-forward.

1. The area must have a large industrial component, with a varied mix of production (steel, chemicals, etc.)
2. The area must be heavily served by the natural gas systems, with an extensive pipeline infrastructure.
3. Proximity to coal fields is desirable, since coal, a near-term option, is one of many potential sources of hydrogen production.

The criteria led to eight major areas in the U.S. being considered. After some additional study of their industrial mix, Pittsburgh, Pennsylvania and its surrounding region was chosen as appropriate for investigation. It is important to note that other areas would have also served for purposes of this study. It is anticipated, however, that the results of this analysis could be transferred to and overlaid upon other regions of the U.S., taking into account possible differences in industrial mix and pipeline structure.

MARKET ANALYSIS

The market analysis involved an examination of the various consuming sectors of the region, considering the traditional use of resources to provide energy services and the potential substitution of hydrogen where appropriate. Examination of the demand sectors in the Pittsburgh area showed significant opportunities for hydrogen use both as a fuel and as a feedstock and industrial commodity. However, for this discussion we will defer the fuel-use opportunities, particularly in the residential and transportation sectors, but keeping in mind that hydrogen can be used for residential heating, particularly when mixed with natural gas, and can be used for transportation fuel providing certain infrastructural changes occur in the future and that reduced disparities between hydrogen and natural gas costs result in a suitable price structure for the fuel mix. The major thrust here, however, was to examine the industrial sector potential for hydrogen considering those areas where it is presently used and where its use can be expanded or substituted for other commodities.

These sectors include:

Iron and Steel
    Direct Reduction Processes
    Annealing

Chemicals
    Fertilizers
    Chemicals and Intermediates
    Plastics

Petroleum Refining

Other Minor Uses
    Glass-making
    Food Processing

Electric Utilities

The estimated total current industrial demand for hydrogen in the market survey region under study is 103,467,000 to 133,479,000 scf/day. The largest portion of this demand is located within a 50 mile radius of downtown Pittsburgh that is heavily served by the natural gas grid. This centralized demand is largely due to the presence of an ammonia plant in Clairton, PA which consumes 65 MMscf/day, a large chemical plant, and an oil refinery. Together these three facilities have the capability to consume over 70 MMscf/day of hydrogen and, because they are closely located in an area heavily covered by gas pipelines in which there are also many small industrial hydrogen users with the potential to consume hydrogen, the hydrogen separation option is feasible from the standpoint of physically delivering the hydrogen to the appropriate industrial customers.

ECONOMIC EVALUATION

The economics of hydrogen supplementation of natural gas are dealt with in very simple terms; supplementation can occur only when an adequate supply of substitute gas becomes available at a price that is the same as or less than the cost of natural gas. Currently, there are no such substitutes because natural gas is the cheapest readily available resource. In the long term (post 2000), it is assumed that natural gas discoveries and production decline, and that consequently natural gas prices rise. As this occurs, hydrogen production costs may also rise, although they could possible drop due to technological innovation. At some point in the future, therefore, the hydrogen and natural gas price curves may intersect. When this occurs, from that point in time onward natural gas and hydrogen basically maintain the same price trajectory. Were this not the case, hydrogen would force natural gas gradually out of the market-place, since the two are essentially interchangeable for end use, taking into account the necessary infrastructural and regulatory change time lags required for hydrogen adaptation.

A major objective of the economic analysis is to pinpoint the time envelope, if any, when economic feasibility of hydrogen supplementation is likely to occur. This approach hinges on forecasted prices of primary resources -- natural gas, coal, and electricity -- for producing hydrogen. In addition, a major task required to evaluate the economic feasibility of hydrogen supplementation in the mid- and long-term future is the estimation of the costs of hydrogen production using conventional technology (steam-methane reforming), and the new developing technologies -- the Shell-Koppers coal gasification process and General Electric's Solid Polymer Electrolyte Process, as examples.

Great uncertainty exists regarding future energy resource supplies and prices which are also influenced by unpredictable worldwide political events. Nevertheless, an attempt was made to estimate the costs of hydrogen production in the period from 1985 to 2020 based on engineering estimates for the three technologies. Forecasted prices of energy inputs are used with these estimates to generate costs of production for 1985 to 2020. Two sets of energy price forecasts (Table 1) are used in the analysis: 1) forecasts from the 1980 Annual Report to Congress[2] (ARC), and 2) a price forecast for natural gas and coal which assume industrial natural gas parity pricing with residual fuel oil, with coal prices linked directly to the world oil price.[3] The use of two forecasts is important in evaluating the effects of uncertainty and in establishing bounds on the estimates.

Table 1
U.S. Average Energy Price Forecasts
(1980 $/MMBtu)

	1965	1973	1978	1985	1990	2000	2020
World Oil Prices[1]-							
$1979/bbl	6.00	6.50	15.50	32.00-43.00	32.00-49.00	42.00- 93.00	58.00-134.00
$1980/bbl	6.54	7.09	16.90	34.88-46.87	34.88-53.41	45.78-101.37	63.22-146.06
Industrial Natural Gas[1]*	0.83	0.82	1.70	5.71- 7.04	4.88- 5.11	5.37- 5.85	6.65- 7.06
F.O.B. Mine Coal - 1980 ARC[1]	0.43	0.61	1.16	1.36- 1.40	1.60- 1.61	1.48- 1.52	1.93- 2.05
F.O.B. Mine Coal - BNL[2]				2.37- 3.17	2.37- 3.61	3.10- 6.83	4.27- 9.83
Industrial Elec. 1980 ARC[1]	7.03	6.39	9.26	13.41-13.73	13.41-14.05	13.72- 14.27	14.01- 14.20
Industrial Elec. BNL[1]**				15.68-17.31	15.37-18.76	17.18- 26.95	18.62- 30.95
Residual Fuel Oil[1]	1.35	1.87	2.71	6.24- 8.14	6.14- 9.21	7.58- 16.24	10.62- 23.06

[1] 1980 Annual Report to Congress - Vol. III, Forecasts, DOE/EIA-0173(80)/3, March 1981. (1979 dollars converted to 1980 dollars using price deflators as follows: 1980 GNP/1979 GNP = 177.36/162.77 = 1.090).

[2] Factors Associated with the Annual Average Price of Bituminous Coal and Lignite, Newcombe, R., and Lamontagne, J., BNL, work currently in progress.

*High priority users, includes industrial surcharge.

**U.S. average electricity prices for industrial customers based on BNL utility coal prices derived from world oil prices.[4]

The hydrogen production costs derived from engineering cost estimates[5] with the two sets of energy price forecasts are summarized in Figure 1. Based on the ARC price forecasts, production costs estimated for the three technologies show that conventional natural gas reforming is currently the least cost process for producing hydrogen, although the margin between natural gas reforming and coal gasification decreases with time. By 1985 coal gasification looks attractive compared to methane reforming. The industrial natural gas demand price (Table 1), however, is significantly lower than the cost of producing hydrogen by methane reforming. Therefore, based on the 1980 ARC energy price forecasts there is no economic incentive for hydrogen supplementation of natural gas in the period 1985-2020. However, based upon the assumptions that natural gas reaches price parity with residual fuel oil and that coal prices track oil prices, Figure 2 shows that hydrogen from both coal and electrolysis may be competitive early in the next century.

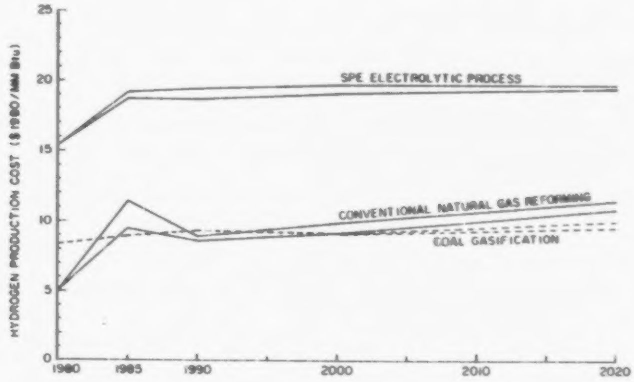

Figure 1
Forecasts of Hydrogen Production Costs Using 1980 ARC Energy Price Forecasts

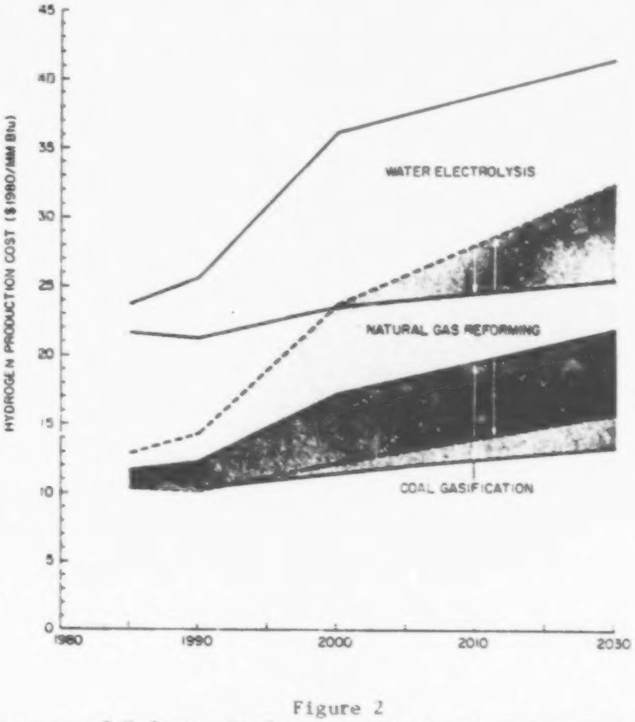

Figure 2
Forecasts of Hydrogen Production Costs Based on Natural Gas Price
Parity with Residual Fuel Oil and Coal Prices Related to World Oil Prices

CONCLUSIONS

- The reassessment of the Natural Gas Supply option suggests no substantive differences in the conclusions of the Ad Hoc Committee.

- The basic concept of hydrogen supplementation of natural gas has no barriers which will impede its evolution. When natural gas supplies dwindle, there is little doubt that supplementation will provide a major, and possibly the only, option in the long-term. The analysis in this study shows that the conditions for this option may appear as early as the year 2000, when hydrogen from coal is the most economic option. Coal is not inexhaustible, and probably in the middle of the twenty first century advanced electrolyzers and solar energy sources will provide the hydrogen needed for both fuel and non-fuel uses. The separation option has more questions associated with it — namely, the economics of the various options vs. natural gas reforming. However, it can also be argued that separation may never be necessary. For example, if hydrogen penetrates the market rapidly, ~~we may~~ switch to an all-hydrogen economy which removes the need for separation.

- Although no barriers exist for hydrogen implementation, there is still a need for R&D to clarify potential problems areas. These areas include economic analysis of hydrogen source options, studies of hydrogen effects on materials, investigations of hydrogen purity requirements for industrial uses, and studies of hydrogen storage options (e.g., ammonia vs. liquid H_2 for small users).

- Hydrogen supplementation of natural gas requires that hydrogen compete with natural gas on an energy basis. Otherwise, rolled-in pricing is required.

- The potential role of hydrogen as a natural gas supplement in the mid- and long-term future is dependent upon future prices of natural gas, coal, and electricity and the supply of natural gas in the United States. Based on current price projections by EIA there will not be an economic incentive for hydrogen supplementation. However, if industrial natural gas prices reach parity with residual fuel oil, hydrogen supplementation will be feasible and, based on EIA projections of residual fuel oil prices, such conditions may occur as early as the 1990 to 2000 time-frame.

- The option of separating "pure" hydrogen from natural gas mixtures at dispersed industrial locations, made possible by hydrogen separation systems such as the metal hydride process currently under development at BNL and other processes under development, is desirable but will not create an overwhelming incentive for the supplementation concept.

- There is strong interest among both current users and potential future users of hydrogen in the option of separating hydrogen from natural gas mixtures as a reliable new supply of hydrogen in the future. The purity of hydrogen does not necessarily need to be extremely high for many of the large hydrogen users in industry; instead, a reliable supply of moderate purity hydrogen that is cost competitive with hydrogen made by steam reforming natural gas is needed.

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PROJECT SUMMARY

Project Title: Hydrogen Recovery from Supplemented Natural Gas

Principal Investigator: Frank B. Hill

Organization: Brookhaven National Laboratory
Upton, New York 11973

Project Goals: Develop a cost effective method for recovery of hydrogen for process use from supplemented natural gas.

Project Status: The process feed and product streams have been defined. Hydrogen recovery techniques were surveyed, and a process employing metal hydrides was selected for study.

$LaNi_{4.7}Al_{0.3}$ was the alloy chosen for the process. A preliminary process design and cost estimate were prepared in which 80 percent hydrogen recovery is attained at a cost of $\$1.40/10^6$ Btu at recovery rates of 1×10^6 SCFD H_2.

Gas-alloy interaction tests were conducted using pure nonhydrogen gaseous components of supplemented natural gas and these components in mixtures with hydrogen. Alkanes did not affect the alloy detrimentally, CO_2 was found to be an inhibitor, and sulfur-bearing odorants were poisons.

The odorant problem is eliminated by taking the process feed from the transmission-distribution system prior to odorant injection. CO_2 inhibition is overcome by the use of pretreatment or enlarged absorption beds.

Contract Number: BNL Prime

Contract Period: October 1, 1980 through September 30, 1981

Funding Level: $130,000

Funding Source: U. S. Department of Energy through Brookhaven National Laboratory

Hydrogen Recovery from Supplemented Natural Gas by Metal Hydrides

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Brookhaven National Laboratory
Department of Energy and Environment
Upton, New York 11973

ABSTRACT

A metal hydride process employing $LaNi_{4.7}Al_{0.3}$ for recovery of hydrogen from supplemented natural gas is being developed. Experimental studies performed to date involved determination of the equilibrium hydrogen capacity of the alloy, measurement of the adsorption behavior of contaminant gases, and measurement of rates of hydrogen absorption by the alloy. The results were used as the basis for a preliminary process design and cost estimate.

INTRODUCTION

The idea of extending natural gas supplies by addition of hydrogen has attracted considerable interest recently. Blends of natural gas with up to 25 percent hydrogen, so-called "supplemented natural gas", would be tolerated by existing transmission and distribution systems and would require little or no change in end use devices. A cost effective process for recovery of hydrogen from supplemented natural gas would provide opportunities for widespread use of hydrogen if and when the use of supplemented natural gas becomes a reality.

This paper describes some development and design work on a hydrogen recovery process based on the use of metal hydrides. These materials selectively absorb hydrogen from mixtures with other gases and subsequently desorb the hydrogen in substantially pure form as the pressure is decreased or temperature increased. They are particularly effective in recovery of hydrogen at the low partial pressures existing in supplemented natural gas since metals or alloys can be found with very low hydride dissociation pressures. Recovery by alternate means, such as pressure swing adsorption or membrane processes, is favored by higher hydrogen partial pressures in the feed stream.

PROCESS PARAMETERS

The feed stream is taken to be a blend of 20 percent hydrogen with natural gas leading to the composition shown in Table 1. The odorants, as will be mentioned below, severely poison the alloy to be used. It is thus desirable to take the feed from the transmission line before its juncture with the distribution system where the odorants are added. The minimum pressure at such a takeoff point is typically 400 psia. This pressure will be taken as the recovery process feed pressure. Hydrogen production rates of interest range from 1 to 100 x 10^6 SCFD.

ALLOY PROPERTIES

In the present work $LaNi_{4.7}Al_{0.3}$ was chosen as the process alloy since it has adsorption pressures which are small compared to a feed partial pressure of, say, 5 atm, at convenient, near-ambient temperatures. Pressure-composition isotherms for this alloy were measured at 25°, 50° and 100° C. The results are shown in Figure 1. From the Van't Hoff relation, the heat of absorption was found to be 8.1 Kcal/gm-mole H_2 in agreement with the values given by Huston and Sandrock.(1) The difference between the absorption and desorption presures is greater in the present work than that reported by Huston and Sandrock.

GAS-ALLOY INTERACTIONS

Studies of the interaction between gas mixture components and the hydriding alloy were carried out to determine the nature of the interaction and to determine parameters of the interaction important for process design. Tests were conducted involving exposures of pure non-hydrogen components to the alloy and of mixtures of these components with hydrogen.

Pure Component Tests. In these tests, the adsorption of pure nonhydrogen components on the alloy surface was measured. Also the effect on the hydrogen absorption rate of exposure of the alloy

Table 1. Composition of Pipeline Natural Gas and of Supplemented Natural Gas

Compound	Composition, percent by volume	
	Pipeline Gas	Pipeline Gas + 20 percent H_2
H_2	0.0	20.0
CH_4	96.3	77.0
C_2H_6	2.1	1.7
C_3H_8	0.4	0.3
$i\text{-}C_4H_{10}$	0.2	0.1
$n\text{-}C_4H_{10}$	0.1	0.1
$i\text{-}C_5H_{12}$	0.1	0.1
$n\text{-}C_5H_{12}$	0.1	0.1
CO_2	0.7	0.6
Odorant[a]	4 ppm	3 ppm

[a] Primarily mercaptans, principally t-butyl mercaptan.

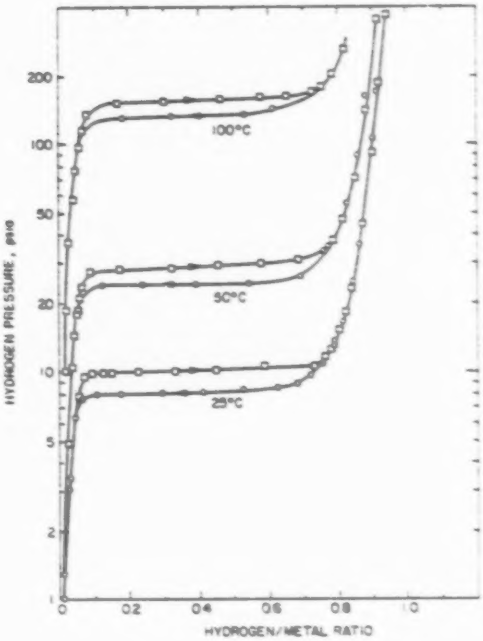

Figure 1. Hydrogen Absorption/Desorption Isotherms for Inco HY-STOR 207, $LaNi_{4.7}Al_{0.3}$ (Heat No. T-84405-2).

surface to such components was measured. For those gases which poisoned the alloy, reactivation was sought by raising the alloy temperature in the presence of hydrogen. Experimental procedures and results are reported in detail in Reference 2. The results important for present purposes are as follows. The alkanes generally do not diminish the hydrogen absorption rate, CO_2 acts as an inhibitor, and the mercaptans are poisons. Regeneration of alloy surfaces poisoned by mercaptans requires exposure to UHP hydrogen at temperatures in the range 260 to 500°C.

Mixture Tests. A schematic diagram of the apparatus for these tests is shown in Figure 2. Two forms of alloy were used: powder and pellets. The powder was Inco HY-STOR 207 with a nominal formula of $LaNi_{4.7}Al_{0.3}$ and heat no. T-84405-2. The pellets which were also made of $LaNi_{4.7}Al_{0.3}$ are proprietary materials developed by an MPD Technology-Air Products joint venture. The reactors were made of stainless steel and contained 2.5 grams of active alloy each.

The temperature of the reactor was maintained constant to within ±0.1°C by means of a constant temperature oil bath. The experimental procedure was as follows:

1. Activate the alloy sample, and then cycle several times with H_2 (Matheson UHP grade with a minimum purity of 99.999% H_2) at the chosen temperature until a steady absorption rate was obtained. This is defined as the baseline or original absorption rate.
2. Cycle with hydrogen-impurity mixtures until a steady absorption rate was obtained.
3. Cycle with hydrogen at the same temperature to investigate the extent of recovery of the original absorption rate.

The ratio of the absorption time immediately following activation to that following subsequent operations was defined as the relative absorption rate.

Three types of operations were conducted: batch, constant pressure and flow-through experiments. The batch and constant pressure experiments were carried out using dead-end reactors. In the batch operations, absorption involved a fixed volume of H_2 in a closed system. Constant-pressure operation involved the same system connected to a live H_2 source maintained at constant pressure. Flow-through experiments were operated at a constant H_2 flow rate and a fixed pressure level.

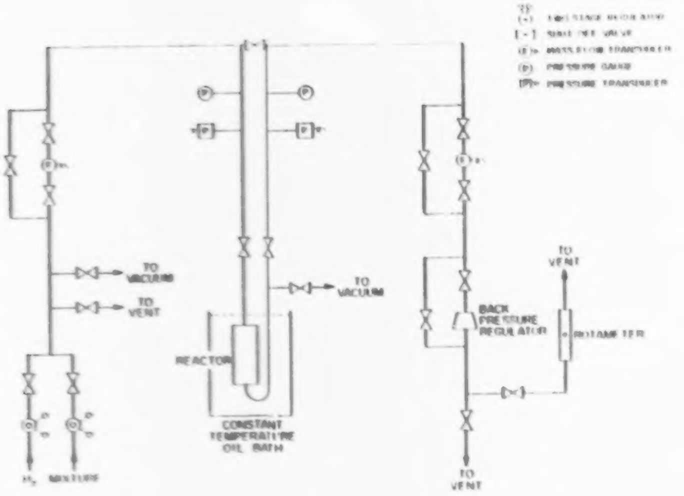
TWO STAGE REGULATOR
SHUT OFF VALVE
MASS FLOW TRANSDUCER
PRESSURE GAUGE
PRESSURE TRANSDUCER
TO VACUUM
TO VENT
TO VACUUM
REACTOR
CONSTANT TEMPERATURE OIL BATH
BACK PRESSURE REGULATOR
ROTAMETER
TO VENT
TO VENT
H_2
MIXTURE

Figure 2. Schematic diagram of experimental apparatus.

H_2-CO_2 Mixtures. Batch contacting experiments on interactions between H_2-CO_2 mixtures and $LaNi_{4.7}Al_{0.3}$ were carried out with repeated cycles of exposure and evacuation at several temperature levels. The relative rate decreased with number of cycles to a steady value usually after about 5 to 10 cycles, a typical result being shown in Figure 3. Following attainment of a steady value, restoration of the original absorption rate was attempted by repeated cycles of exposure to H_2 and evacuation. As shown in Figure 3, an increase in relative rate was obtained which leveled off after about 3 to 4 cycles. Results of a series of such experiments are shown in Table 2, where "ultimate evacuation pressure" means the final equilibrium pressure in the evacuation part of the cycle. Only batch experiments were conducted. Both alloy powder and pellets were tested.

One striking point as seen from Table 2 is that for the alloy powder, the original rate was completely recovered when using a 16 psia ultimate evacuation pressure whereas only partial recovery was effected at 0.1 torr. However, for alloy pellets, the original rate was not fully recovered with the 16 psia ultimate evacuation pressure at 50°C but was completely recovered with 0.1 torr at 100°C. It seems that the ultimate evacuation pressure has a stronger effect on the alloy powder than it has on the pellets and the temperature has just the opposite effect. In all cases, a higher temperature, a higher evacuation pressure and a lower CO_2 concentration increase the hydrogen absorption rate.

It is also seen from Table 2 that much higher absorption rates were obtained with pellets than with powder either with H_2 or with mixtures. This fact is consistent with the principles underlying the design of the pellets.

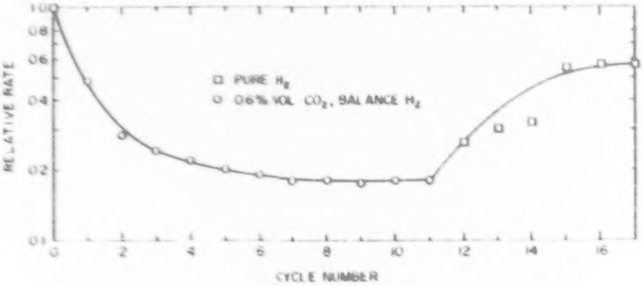

Figure 3. cyclic test of $LaNi_{4.7}Al_{0.3}$ powder at 100°C.

Table 2. Effect of CO_2 on H_2 Absorption Rate---Batch Exeriments

A. UHP H_2 absorption for freshly activated alloy

T, °C	Initial H_2 partial pressure, psia	Absorption rate (r_o), $\Delta(H/M)/min^a$	
		powder	pellets
1. Ultimate evacuation pressure (P_{ev}) < 0.1 torr			
25	89	0.405/0.27	---
50	89	0.405/0.78	0.663/0.11
100	180	0.095/0.43	0.316/0.98
2. P_{ev} = 16 psia			
50	90 (powder), 80 (pellets)	0.429/1.08	0.66/0.6
75	142	0.406/1.4	0.58/0.58
100	180	---	0.28/0.55

B. Absorption of H_2 from H_2-CO_2 mixtures (y_{CO_2}=0.6%, except as noted)

T, °C	H_2-CO_2 mixture		UHP H_2	
	No. of cycles for steady rate	$\frac{r}{r_o}$	No. of cycles for steady rate	$\frac{r}{r_o}$
1. P_{ev} < 0.1 torr				
powder				
25	13	0.075	4	0.41
50	11	0.132	5	0.566
100	5	0.41^b	3	0.57
100	7	0.18	5	0.57
pellets				
50	14	0.207	10	0.63
100	16	0.59	5	1.00
2. P_{ev} = 16 psia				
powder				
50	4	0.20	6	1.00
75	8	0.32	5	1.00
pellets				
50	15	0.217	14	0.63
75	6	0.65	7	0.93
100	5	0.67	3	1.00

[a] Actual absorption time.

[b] y_{CO_2} = 0.2 %

H_2-CH_4 Mixtures. The results for these tests are presented in Table 3 for alloy powder and in Table 4 for pellets. In batch experiments with powder, it is seen from Table 3 that the steady relative rate is strongly affected by the CH_4 concentration. Since CH_4 does not interact with the alloy, the reduction in absorption rate should be due to mass transfer resistances. To confirm this, experiments were carried out with pellets under batch, constant pressure, and flow-through conditions as described before. As shown in Table 4, the hydrogen absorption rate increases from batch to flow-through conditions not only with H_2 but also with the mixtures. With H_2, the change was small because any diffusion limitation or mass transfer resistance is small. However, the improvement of the hydrogen absorption rate was dramatic with H_2-CH_4 mixtures, especially at higher CH_4 concentrations. Under flow-through conditions, the absorption rates with mixtures were about the same as with H_2, indicating that mass transfer resistance or diffusion limitation was almost completely eliminated.

Table 3. Effect of Methane on H_2 Absorption Rate---Alloy Powder

Batch experiments

Ultimate evacuation pressure = 16 psia
Initial H_2 partial pressure = 144 psia

T, °C	y_{CH_4}, %	UHP H_2	H_2-CH_4 mixture
		r_o, Δ(H/M)/min[a]	r/r_o
60	10	0.265/0.123	0.013
60	50	0.265/0.127	0.00015
75	0.6	0.406/1.03	0.954
75	10	0.265/0.38	0.0122

[a] Actual absorption time.

Table 4. Effect of Methane on H_2 Absorption Rate---Alloy Pellets

Ultimate evacuation pressure < 0.1 torr

T, °C	y_{CH_4}, %	H_2 absorption rate, Δ(H/M)/min[a]	
		UHP H_2	H_2-CH_4 mixture
Batch (Initial H_2 partial pressure = 80 psia, except as noted)			
50	10	0.71/0.5	0.486/0.5
50	—	0.74	—
75	10	0.526/0.07[b]	0.526/0.38[b]
75	10	0.27	0.197
75	50	0.27	0.062
Constant pressure (Feed H_2 partial pressure = 80 psia)			
50	10	0.762/0.5	0.586/0.5
75	10	0.47	0.234
75	50	0.47	0.084
Flow-through (H_2 partial pressure = 80 psia, flow rate = 300 SCCM)			
50	10	0.762/0.5	0.753/0.5
50	—	0.77/30	—
75	10	0.47	0.44[c]
75	50	0.47	0.475[c]

[a] Actual absorption time: one minute, or as shown.
[b] Initial H_2 partial pressure = 138 psia.
[c] Slightly different operating conditions.

As seen in Table 4, most of the equilibrium capacity was reached in the first minute of absorption under flow-through conditions. This suggests that a short absorption cycle time may be employed.

PROCESS DESIGN AND ECONOMICS

Based on the experimental work described above, a preliminary process design was prepared. The principal process components consist of a pretreatment section and a hydrogen recovery section as shown in Figure 4. Pretreatment is definitely required if mercaptans are present. If mercaptans are absent pretreatment may be required to reduce the CO_2 concentration prior to hydrogen absorption.

Alternately, larger absorption beds may be used to overcome the reduced rates brought about by the presence of 0.6 percent CO_2. The choice of our approach or the other will depend upon cost estimates yet to be made. It is likely that the pretreatment option will be less expensive.

The pretreatment scheme shown is for removal of either mercaptan or CO_2 and would involve adsorption with an adsorbent appropriate for the species of interest. A two-bed system is shown. One bed is on line while the other is being regenerated.

The hydrogen recovery section consists of two beds of $LaNi_{4.7}Al_{0.3}$ pellets, one absorbing and the other desorbing. A third bed may be necessary if further work discloses that a long desorption time is required.

Cost estimates for hydrogen recovery were prepared using the Lang factor method (References 3 and 4) and assuming an alloy cost of $10/lb, 80 percent hydrogen recovery, 70 percent utilization of the alloy capacity, and carbon steel as the material of absorber construction. The cost of any required regeneration is not included.

Results of the cost estimation work are given in Table 5. While the base case cost of $\$1.40/10^6$ Btu appears to be at least competitive with the costs of other hydrogen recovery methods, including membrane processes and pressure swing adsorption processes, the final cost is expected to be higher. Hence it is too soon to pass judgement on the process based on cost consideration.

Cost sensitivities are shown in the lower half of Table 5. The cost is highly sensitive to the concentration of hydrogen in the feed and to the presence of odorants. It is only weakly sensitive to production rate and feed pressure.

CONCLUSION

Experimental studies of interactions of the components of supplemented natural gas with $LaNi_{4.7}Al_{0/3}$ have shown the following.

(a) Alkanes were physisorbed by the alloy and did not detrimentally modify surface behavior. An external mass transfer resistance was evident in the absorption of hydrogen from H_2-CH_4 mixtures. This resistance was greatly reduced in a flow system.

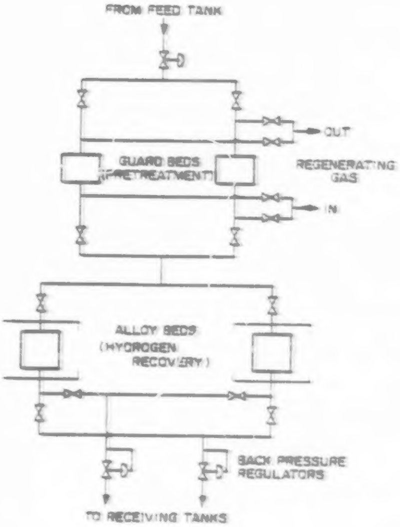

Figure 4. Process flowsheet (conceptual).

Table 5. Preliminary Estimates of Cost of Hydrogen Recovery

Base case		
H_2 concentration in feed	20%	
Feed pressure	400	psia
H_2 recovery rate	1×10^6	SCFD
Mercaptan concentration in feed	0	ppm

Factor	Change in Base Case Cost, %
H_2 concentration in feed = 10%	+120
Feed pressure = 1000 psia	- 3
H_2 recovery rate = 10×10^6 SCFD	-12
Mercaptan concentration in feed = 1 ppm	+ 64

(b) CO_2 was chemisorbed by the alloy and it acted as an inhibitor to hydrogen absorption. Inhibition was evident in a reduced rate of absorption that was temperature dependent.

(c) Mercaptans poisoned the alloy with respect to hydrogen absorption, blocking absorption altogether. Regeneration was possible by exposure of the alloy to hydrogen at a temperature between 260°C and 500°C.

Preliminary cost estimates of a recovery process based on these findings indicate a hydrogen recovery cost of $\$1.40/10^6$ Btu, competitive with other recovery schemes.

ACKNOWLEDGEMENT

The authors express appreciation to Rodney M. Richter for expert experimental assistance.

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CHEMICAL HEATPUMP

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PROJECT SUMMARY

Project Title: Sulfuric Acid/Water Chemical Heat Pump

Principal Investigator: E. C. Clark

Organization: Rocket Research Company
Redmond, Washington
(206)885-5000

Project Goals: The project is structured to verify the capability of the sulfuric acid-water system. The primary objective is to design, construct and test a sulfuric acid CHP/CES verification test unit (VTU) which incorporates as many commercial, mass producible design features as necessary to demonstrate system economic and technical feasibility. The VTU will be designed to function both as a storage HVAC unit and a temperature enhancement industrial heat pump. For purposes of gaining scaling criteria, the nominal storage design capacity shall be 10^6 Btu with a nominal delivered heat rate of 150,000 Btu/hr.

Project Status: Rocket Research is currently under contract to Brookhaven National Laboratory to conduct a four-phase program. Phases I, II and III have been completed and consisted of a requirement analysis, detailed design, and fabrication of the VTU. Generic applications have been identified which include industrial waste heat pumping, space conditioning, air or gas moisture removal, steam accumulation, cogeneration and energy storage. The VTU design incorporates two of the above designs: waste heat pumping and space conditioning. The design incorporates combined generator/condenser and absorber/evaporator reaction components made of steel shells coated with acid-resistant porcelain. Teflon-lined acid plumbing and valves have been used and the acid storage tank is fabricated from steel lined with porcelain and capable of vacuum operation.

The remaining Phase IV test program has been initiated and is currently in progress.

Contract Number: 494588-S

Contract Period: 1 October 1979 through September 1981

Funding Level: $699,740

Funding Source: U.S. Department of Energy/Brookhaven National Laboratory

THE SULFURIC ACID/WATER CHEMICAL HEAT PUMP/ENERGY STORAGE PROGRAM

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ABSTRACT

A sulfuric acid chemical heat pump/energy storage verification test unit (VTU) has been designed, fabricated and is presently being tested under the current Phase III program. The power rating is 150,000 Btu/hr and the unit is capable of storing 1 x 10^6 Btu. The VTU has been designed to operate in two modes: an industrial chemical heat pump for temperature enhancement (amplification) of reject heat and an HVAC unit for space conditioning (heating and cooling) with energy storage. Economic studies conducted during the program have resulted in the selection of the industrial chemical heat pump as the primary emphasis for testing. Equipment payback periods of 1 to 3 years are estimated, based on system size.

The engineering model system developed under the previous Phase II and II-A(2,3) contracts was tested during the current contract to continue the study of component life and system configuration.

INTRODUCTION

Chemical heat pumps represent a new technology base with the ability to substantially reduce the consumption of energy in the industrial, commercial and residential sectors. These devices provide an ability to capture low-grade heat rejected from buildings and industrial sources and to reuse the heat at increased temperature levels for comfort and water heating or in industrial processing. Chemical heat pumps operate with up to 15 times less electrical power and in higher temperature regimes than conventional heat pumps, thus affording significant performance advantages over the conventional designs. An additional advantage is that energy storage can be incorporated because of the working fluid selection so that intermittent energy sources, such as solar energy, can be utilized. It has been conservatively estimated that chemical heat pumps can eventually displace 0.2 quads (35.7 million barrels of crude oil) annually. The distribution of this energy is equally divided between utilization of reject industrial process heat and commercial/residential solar-driven heating and cooling units. This reduction of crude oil consumption represents a reduction of foreign imported oil equalling $1.2 billion per year (at $35/barrel).

SYSTEM OPERATION

To illustrate the Industrial Chemical Heat Pump (ICHP) operation, it is possible to draw a simplified schematic which describes the flow of heat in and out of the system. Figure 1 presents the generic ICHP schematic for the sulfuric acid/water system. The four reaction components are shown without storage. The acid circuit is continuous, with the dilute acid input into the generator where the concentration process takes place using flash distillation.

The concentrated acid is routed to the absorber where the acid dilution process takes place, releasing the heat of vaporization of water (vapor from evaporation) plus the heat of dilution. Heat is removed from the condenser at low temperature, and the waste heat is input into the evaporator with the water vapor always flowing from the generator to the condenser or from the evaporator to the absorber For the ICHP, waste heat is also supplied to the concentrated acid stream, and heat is withdrawn for process needs at a higher temperature from the dilute acid stream. Since the generator and condenser as well as the absorber and evaporator are pair-wise in vapor communication, the pressure of each combined component is regulated by the temperature at which water is condensed or evaporated. For the ICHP, waste heat is input into the evaporator at a temperature much higher than that temperature at which heat is withdrawn from the condenser. Therefore, the absorber/evaporator pressure (Pe) is higher than the generator/condenser pressure (Pc).

The heat balance for the system is:

$$Q_{in(acid)} + Q_{in\ (evaporator)} = Q_{out\ (acid)} + Q_{out\ (condenser)}$$

This assumes that the water leaves the condenser and enters the absorber at the same temperature.

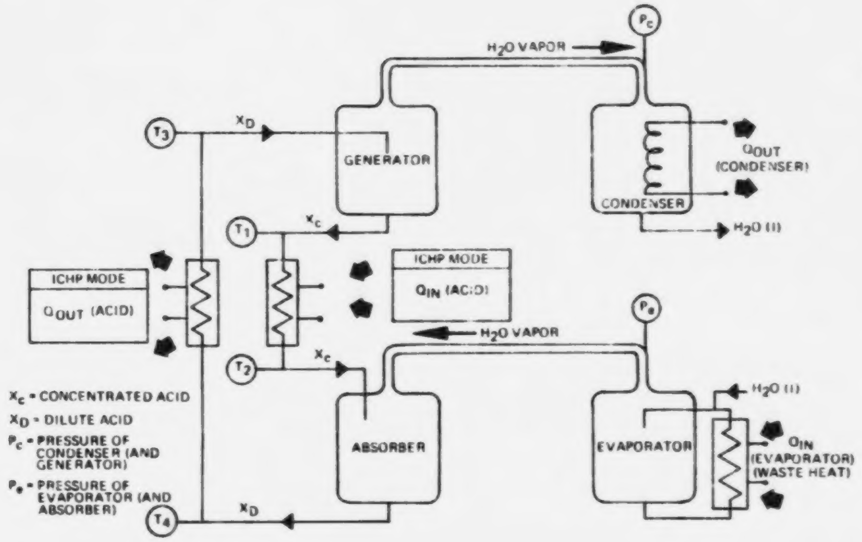
P_c
H_2O VAPOR
T_3
X_D
GENERATOR
CONDENSER
Q_{OUT} (CONDENSER)
H_2O (l)
T_1
X_c
ICHP MODE
Q_{IN} (ACID)
ICHP MODE
Q_{OUT} (ACID)
P_e
H_2O VAPOR
T_2
X_c
H_2O (l)
ABSORBER
EVAPORATOR
Q_{IN} (EVAPORATOR) (WASTE HEAT)
X_c = CONCENTRATED ACID
X_D = DILUTE ACID
P_c = PRESSURE OF CONDENSER (AND GENERATOR)
P_e = PRESSURE OF EVAPORATOR (AND ABSORBER)
X_D
T_4

Fig. 1. Generic Industrial Heat Pump Schematic

Since water is being evaporated and condensed, the magnitude of $Q_{in(evaporator)}$ and $Q_{out(condenser)}$ is approximately the same. Therefore, the magnitude of $Q_{in(acid)}$ and $Q_{out(acid)}$ is also approximately the same.

In Figure 1 the liquid water output from the condenser is not shown connected to the evaporator input because in many cases the water circuit can be an open cycle. For example, when using low pressure water steam vented to the atmosphere, the steam can be routed to the absorber directly, bypassing the evaporator. The water condensate would then be pumped from the vacuum-operated condenser and discharged into a sewer.

Further explanation of the ICHP thermodynamic considerations is provided in reference 5.

PERFORMANCE

The performance of industrial heat pumps is typically defined as an electrical coefficient of performance (COP_e) rather than the total energy version. Essentially the heat extracted from the energy supply source is not considered for performance evaluation since it would normally be rejected. The parasitic work required to drive the equipment is converted directly to thermal units without the three-to-one electric power conversion efficiency. Therefore, COP_e is defined as:

$$COP_e = \frac{Q_{out}}{W_{parasitic}}$$

where:

Q_{out} = heat rate (Btu/hr) to the hot process

$W_{parasitic}$ = electrical power (Btu/hr) required to pump water and acid through the ICHP and heat exchangers

The above COP_e is useful in determining ICHP operational costs for calculation of system payback. The industrial user is also concerned with the quantity of reject heat which must be supplied to produce the benefits of the process heat. For this reason, the thermal COP_t must be considered as follows:

$$COP_t = \frac{Q_{out}}{Q_{in}} \quad \left(\frac{Q_o}{Q_I}\right)$$

where:

Q_{in} = heat rate (Btu/hr) supplied to the system (acid plus absorber) by the waste heat stream

Knowing the above ratio, the industrial user can determine if sufficient reject heat is available, and determine if the installation costs will be reasonable as well as define any positive or negative contribution to the operational cost.

ICHP's can be optimized for particular applications. A single reject heat source can be used to supply energy to the evaporator and the concentrated acid heat exchanger. Calculated COP_e as a function of the waste heat source temperature is presented in Figure 2 for various values of COP_t. Assumptions for these calculations were a condenser inlet temperature of 50°F, parasitic power for the pumps, and a process water temperature rise of 20°F. Also shown cross-plotted is the maximum temperature delivered to the process. As the waste heat source temperature is increased, the COP_e increases. Typical values for COP_t range from 0.5 to 0.1. Thus, the reject heat supply must be from 2 to 10 times larger than the process needs. Note that temperatures as high at 380°F with reject heat temperatures of 240°F, can be produced but at substantially reduced COP_e and COP_t. In this case, values of COP_e range from 46 to 5, with corresponding Q_o/Q_I ratios of 0.5 to 0.1.

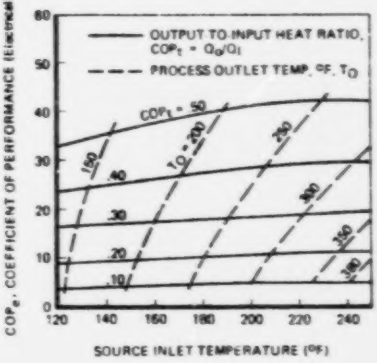

Fig. 2. Performance of Industrial Chemical Heat Pump

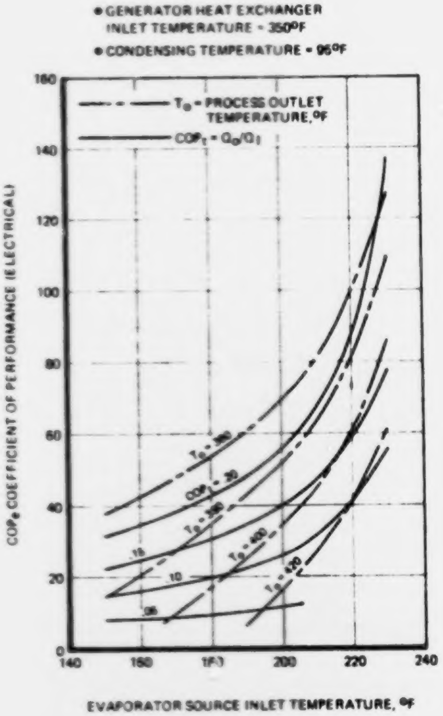

Fig. 3. Performance of Industrial Chemical Heat Pump with Two Reject Heat Sources

Figure 3 presents the performance of an ICHP operating with two reject heat sources. In this example, a moderately high reject heat source is used to drive the generator heat exchanger (reference Figure 1 heat exchanger operating with concentrated acid) while a lower reject heat source is used to drive the evaporator. A condenser temperature of 95°F was chosen because a cooling tower will most likely be used in most industrial applications. The temperature of the fluid used to extract heat from the higher temperature reject heat source is assumed to be 350°F when returning to the acid heat exchanger. As shown in Figure 3, in the case where the waste heat stream temperature supplied to the evaporator is 210°F (located on Figure 3 abscissa), energy can be delivered to the process at 360°F to 420°F which will provide 100 psig and 230 psig steam, respectively. Correspondingly, electrical COP_e ranges inversely from 27 to 80. In a similar manner, the system thermal COP_t ranges inversely from 0.09 to 0.25.

VTU DESIGN AND FABRICATION

A verification test unit (VTU) has been designed and is capable of two operational modes: (1) industrial chemical heat pumping, and (2) heating, ventilation and air conditioning (HVAC) with energy storage. The design incorporates low cost, readily available engineering materials which are packaged in a commercial-type configuration. The unit is easily scaled, and is designed with ease of maintenance and operator safety in mind. The nominal power rating is 150,000 Btu/hr, with a storage capacity of 1×10^6 Btu. To date, fabrication and assembly are complete, and the test program is in progress.

Figure 4 shows a photograph of the completed unit. The VTU was designed with both horizontally integrated combined generator/condenser and absorber/evaporator reaction components. The horizontally integrated design is both compact and adaptable to scaling. The reactors are fashioned from 18-inch-diameter pipe closed at one end by a welded elliptical end cap, and closed at the access end with an ASME-rated flange. The interior of the pipe and end cap are completely lined with vitreous porcelain enamel. The lower half of the reactor contains a reaction tray, also porcelain-coated. The tray eliminates the need to enamel the closure plate as well as giving redundant containment for the acid. Additionally, the tray can be readily replaced, if necessary, at about 15 percent of the cost of replacing the entire reactor shell. Both the generator section and the condenser assembly, as well as the evaporator/absorber, are removable for inspection or component change or replacement, and are designed to interface with standard acid and water plumbing.

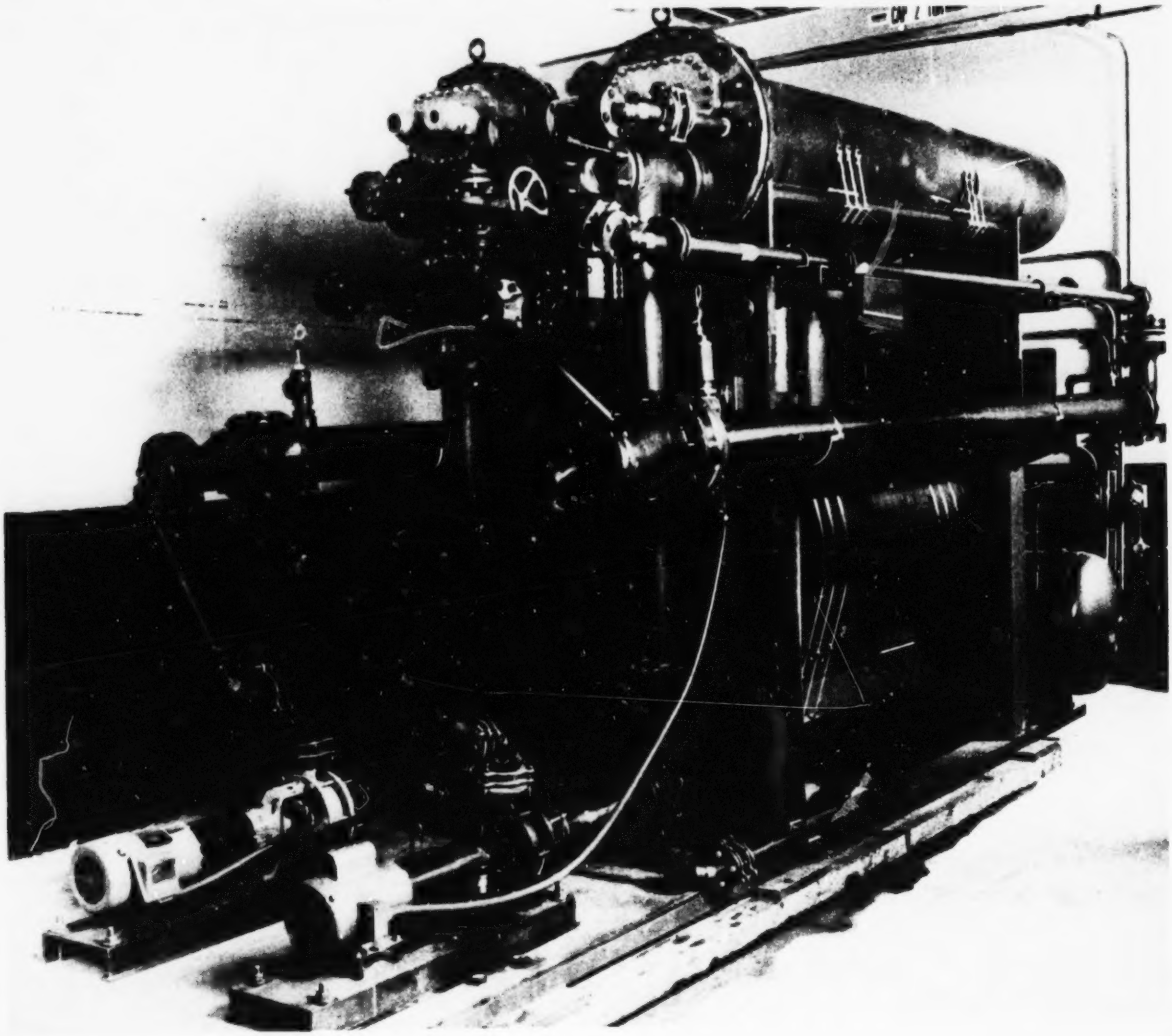

Fig. 4. Completed VTU

Acid service heat exchangers were designed by RRC in response to requirements imposed by the VTU which exceed design limits of existing commercial units. Low-cost readily available hardware and common materials of construction were used throughout to create a heat exchanger with higher performance limits and lower costs than competing brands. Each heat exchanger contains 60 square feet of surface area with 31 Pyrex glass tubes, Carpenter 20 Cb-3 tube sheets, and Kalrez O-rings on the acid side.

Acid and water storage tanks were designed for the VTU. Each tank is ASME pressure rated and each is fully vacuum capable. The acid tank is located low on the support frame to allow gravity drainage from the rest of the system components.

The acid plumbing string for the VTU has been configured in Teflon-lined pipe and clamp valves; water plumbing is black iron pipe. A natural gas-fired boiler was selected to simulate the waste heat source. A combination flash and hot-water storage tank was added, as the boiler has no storage.

The main frame is a steel structure which is bolted together. It is symmetrical about the longitudinal axis and therefore adapts to a right- or left-hand floor plan without change. The heat exchangers are supported by U-shaped brackets padded with Teflon to cushion the components and allow them to slide into place. The reactors and acid tank are supported by Teflon-lined brackets and I-beams. Both the reactors and the heat exchangers are canted to promote drainage.

Raw material procurement and subcontractor selection was completed with few problems. Durco high-silicon iron, used for the heat exchanger tube sheets, required lead times of about 5 months so Carpenter 20 plate, available off-the-shelf, was substituted. Carpenter 20 is not as corrosion resistant as Duriron, particularly between 60 and 75 Wt % H_2SO_4, but ample corrosion margin was allowed during tube-sheet design.

The larger components, in particular the reactors, reaction trays, acid tank, and main frame were fabricated by local contractors. The porcelain lining was also applied by a local firm. Parts were made to print, and deliveries were on schedule; however, a problem was encountered with the reaction trays. During the several firings associated with porcelain coating, the trays slumped to such an extent that they would not fit in the reactor. The trays were repaired by mechanically pressing them back into shape, firing them in an annealing oven and recoating with porcelain.

VTU TESTING

The VTU test program is currently in progress. Initial leak checks, fill and drain, and startup procedures have been completed. Temperature amplification has been demonstrated initially with the system uninsulated. Acid temperatures of 208°F were achieved for a simulated reject temperature source input of 180°F. A process outlet temperature of 200°F was measured. Acid concentration was nominally 55 percent by weight. Successful operation of the generator was also demonstrated, although not simultaneously.

Three equipment problems have prevented successful continuous cycle operation thus far: vacuum leaks, retention of the column packing in both the generator and absorber, and collapse of the Teflon liner in the 4-inch-diameter acid plumbing. The vacuum leakage occurred in the generator during the successful temperature amplification runs. The leakage was largely due to initial temperature cycles and has been corrected by retorquing the system flanges. The remaining two problems reduced system acid flow and caused liquid holdup in both the generator and absorber. The loss of liquid in the system plumbing caused cross-pressurization between the generator and absorber, therefore stopping the acid concentration and continuous cycling. Currently, the generator and absorber are being disassembled and the bed retention problem fixed by design change. The 4-inch-diameter Teflon-lined pipe has been returned,without additional cost to the manufacturer and has been replaced with new units with special vacuum ports for balancing pressure across the lining. The special vacuum units were not advertised by the manufacturer as necessary nor were they referenced by the sales representative during procurement. Other manufacturers do not require pressure balancing and will be recommended for future procurement.

Testing will resume once the absorber and generator are reassembled. Performance mapping with measurement of system COP will occur at that time.

CONCLUSION

The sulfuric acid chemical heat pump has been shown to be a cost-effective device with a large potential for fuel savings as an industrial reject heat recovery device and for building heating and cooling with energy storage. Equipment payback in the industrial unit is very short with longer paybacks estimated for the heating and cooling units. A verification test unit (VTU) has been successfully undergoing testing. The VTU uses low-cost components and construction techniques. Demonstration of temperature amplification in the industrial heat pump mode has been successfully achieved. Equipment shakedown testing is in progress with performance mapping and COP measurements to be accomplished in the near future.

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PROJECT SUMMARY

Project Title: Chemical Heat Pump Cost-Effectiveness Evaluation

Principal Investigator: Warren R. Standley

Organization:
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Project Goals: The objective of this study was to compare the cost effectiveness and energy effectiveness of existing chemical heat pump (CHP) concepts with a baseline of conventional energy technologies and a group of near-term emerging energy technologies with which CHPs are expected to compete. The analysis was structured to evaluate these systems functioning as the primary space conditioning unit of both a "standard" single-family detached home and a "representative" commercial building. Each HVAC system and application was analyzed in each of two locations in the United States, the southwest (Albuquerque, NM) and the northeast (Boston, MA). In addition, the CHPs were evaluated in two "representative" industrial waste heat upgrading applications, and compared to potentially-competitive technologies for industrial "heat pumping."

Project Status: The Energy Engineering Division of TRW has conducted a comparative economic and energy consumption evaluation of chemical heat pumps (CHPs) in support of the Chemical/Hydrogen Energy Storage Systems Program at Brookhaven National Laboratory (BNL). CHPs extract thermal energy from a low-heat temperature source and reject it to a higher-temperature sink. Unlike vapor-compression heat pumps, chemical heat pumps make use of reversible chemical reactions between a working fluid (or vapor) and one or more stationary phases (solid or liquid). Chemical heat pumps are being developed by DOE and BNL because they offer the promise of lower overall cost and greater efficiency than separate units for heating, cooling, and (in solar operations) storage. They are also being considered for industrial process heat upgrading applications. In these roles, CHPs must compete successfully on economic levels with present-day baseline systems and with near-term emerging technologies. The study described in this paper addresses both aspects of the comparison, that is, the cost effectiveness and energy resource effectiveness of CHPs.

Under contract to Brookhaven National Laboratory, TRW conducted a cost-effectiveness and energy resource evaluation of two chemical heat pump (CHP) concepts: a sulfuric acid-water CHP and a methanol-calcium chloride CHP. The CHPs were compared to baseline and emerging competitive technologies for providing space conditioning services to residential and commercial buildings and for upgrading industrial process heat, using levelized annual cost as the measure of cost effectiveness. The study concluded that CHPs could be cost effective and conserve energy resources in applications for industrial process heat upgrading and, in specific applications, for residential heating and cooling. CHPs for commercial office building space conditioning are neither resource nor cost effectiveness.

Contract Number: 519403-S

Contract Period: June 1980 through March 1981

Funding Level: $98,345

Funding Source: Department of Energy

CHEMICAL HEAT PUMP COST EFFECTIVENESS EVALUATION

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OBJECTIVE

The objective of this project is to compare the cost-effectiveness and energy-effectiveness of existing chemical heat pump (CHP) concepts with a baseline of conventional energy technologies and a group of near-term emerging energy technologies with which CHPs are expected to compete. The analysis is structured to evaluate these systems functioning as the primary space conditioning unit of both a "standard" single-family detached home and a "representative" commercial building. Each HVAC system and application is analyzed in each of two locations in the United States, the southwest (Albuquerque, NM) and the northeast (Boston, MA). In addition, the CHPs are evaluated in a "representative" industrial waste heat upgrading application, and compared to potentially-competitive technologies for industrial "heat pumping."

BACKGROUND

A chemical heat pump is a device that extracts thermal energy from a low-temperature source and rejects it to a higher-temperature sink. Unlike vapor-compression heat pumps which use the vapor-liquid phase characteristics of a single working fluid, chemical heat pumps make use of reversible physiochemical reactions between a working fluid (vapor) and one or more stationary phases (solid or liquid). Chemical heat pumps are being developed by DOE because they offer the promise of lower overall cost and greater efficiency than separate units for heating, cooling, and (in solar operations) storage. They are also being considered for industrial process heat upgrading applications.

Chemical heat pumps must compete with existing HVAC and industrial process-heat technologies; including gas and oil-fired furnaces, vapor-compression heat pumps, and vapor-compression air conditioners. In addition, they will compete with emerging technologies such as solar-thermal heating, solar-driven absorption air conditioning, and ground or aquifer-coupled vapor-compression heat pumps. An applications-specific comparison between the chemical heat pump systems, the baseline systems, and the emerging technologies will enable the promised benefits of the CHP's to be weighed against the cost of ownership and operation.

Methodology. A characterization of building type and pattern of use, as well as detailed location-specific climatic data, were used to determine the annual energy requirements for each HVAC application and location. The energy requirement in the industrial application was assumed to be one-million Btu/hr. for each of two end-users, process steam and process hot water. The annual fuel cost, system cost, and maintenance cost were determined based on the technical definition of a specific energy system in a given application. Levelized annual cost, based on constant-dollar calculations, was selected as the economic criterion for making cost-effectiveness comparisons between CHPs and competing systems. For the purpose of this study, the "constant-dollar" interest rates were taken to be 2 percent for home-owners and 6 percent for businesses; with annual fuel price escalation rates of 0.6 percent for electricity, 2.6 percent for distillate fuel, and 3.2 percent for natural gas.

Residential Space-Conditioning. The "standard" single-family detached home is assumed to be a single-story structure with 1500 square feet of floor space. The building meets the energy conservation standards of ASHRAE 90-75, and is considered to be typical of the well-insulated dwellings which will characterize the future new home market which CHPs might penetrate. The baseline space-conditioning systems for residential applications include:

- Gas-fired furnace with electric air conditioning
- Oil-fired furnace with electric air conditioning
- Electric heat pump with electric-resistance backup heating

The near-term, emerging technologies for residential HVAC include:

- Solar heating with electrically-driven air conditioning (gas, oil, or electric backup for heating)
- Solar-assisted heat pump with electric backup and electrically-driven air conditioning
- Ground-coupled heat pump
- Solar heating with gas backup and solar-absorption air conditioning

Commercial Space-Conditioning. The "representative" commercial building is assumed to be a three-story structure with 40,320 square feet of floor space. This building also meets the energy conservation standards of ASHRAE 90-75, with a well-designed building envelope to minimize solar loads and regenerative heat exchange to reduce ventilation-associated loads. The space-conditioning requirements of the commercial building were assumed to vary according to the pattern of use. The baseline space conditioning systems for the commercial application include:

- Gas-fired boiler with electrically-driven air conditioning
- Electric boiler with electrically-driven air conditioning

The near-term, emerging technologies for commercial HVAC include:

- Solar heating with electrically-driven air conditioning (gas backup or electric backup for heating)
- Solar-assisted heat pump with electric backup and electrically-driven air conditioning
- Ground-coupled heat pump
- Solar heating with gas backup and solar-absorption air conditioning

Industrial Waste-Heat Upgrading. Two industrial waste-heat upgrading applications were established as the basis for comparing CHPs to other industrial heat pumping systems. The primary application involves producing one-million Btu/hr of 300°F, 67 psia process steam, given a supply of 220°F waste water and 50°F cooling water. A secondary application involves a one-million Btu/hr demand for reheating a process-water stream from 240°F to 260°F, given a supply of 210°F waste water and 50°F cooling water.

The analysis of chemical heat pumps in applications for upgrading industrial waste heat to process heat requires comparison to some alternative energy system. The natural comparison is to a fired boiler of the same thermal rating or a competitive industrial heat pump system. For the upgrading of waste heat pump technologies which are feasible with state-of-the-art equipment: (1) the Westinghouse Templifier, and electrically-driven Rankine cycle heat pump with Freon working fluid, and (2) a steam vapor-compression system. For the purpose of this study, industrial CHPs are compared to four alternative systems, including:

- Fired steam boiler
- Westinghouse Templifier heat pump
- Electrically-driven vapor recompression
- Steam-driven vapor recompression

CHP Systems Evaluated. The Sulfuric acid CHP being developed by Rocket Research Company and the methanolated-salt CHP being developed by EIC Laboratories were compared to the baseline and emerging technologies described above. A hydrogen-metal hydride CHP which is under development by Southern California Gas Company was not evaluated because manufacturer-supplied performance and cost data are not available at this time.

SUMMARY

In residential HVAC applications, the role of either CHP concept in energy conservation is best served through solar-driven applications, the economics of which are somewhat better than baseline and emerging systems. Direct-fired CHPs are less expensive to own and operate, but are not a good approach to energy conservation. Given the increased complexity of the sulfuric acid system and the barriers to commercialization (safety, institutional, and customer-psychological), the methanolated salt system would probably be the most attractive CHP technology for residential use. Because of the dominance of the air conditioning load, use of either CHP for heating and cooling a commercial office building would be very expensive, competing only with the most expensive emerging systems. Since this use of CHPs is also not very attractive from an energy standpoint, there appears to be little incentive for CHPs in HVAC applications in commercial buildings.

The industrial CHPs were found to be more cost-effective to own and operate than an electrically-driven vapor recompression system because of the high energy cost for electricity. CHPs were most cost-effective than the self-driven vapor recompression system because of the high capital cost of the power-recovery turbine capable of exhausting to very low pressure. The only commercially-available industrial heat pump, the Westinghouse Templifier, is constrained to temperature levels below 230°F, and is not considered to be a serious competitor for process heat applications in the temperature range of interest to BNL.

TECHNICAL ACCOMPLISHMENTS

- In HVAC applications, not all CHP systems are energy-conservative when compared to the baseline (existing) technologies. The value of CHPs in energy resource conservation is both application and location specific. Each solar-driven CHP system consumes fewer energy resources than the competing baseline and emerging systems. (In this context, energy resources reflect the primary resource consumed to produce and deliver the energy requirement of the end-use system.) The residential application of a gas-fired CHP in a Northeast location (Boston), is more energy-conservative than the baseline systems, but not the emerging systems. The dominance of the air conditioning load for a commercial building in both locations and for the residence in the Southwest (Albuquerque) makes the gas-fired CHP systems much less energy efficient than the emerging technologies and somewhat less energy-efficient than baseline systems. The annual energy-resource consumption of both CHPs and competing systems is illustrated by Figure 1 for residential systems and Figure 2 for commercial systems.

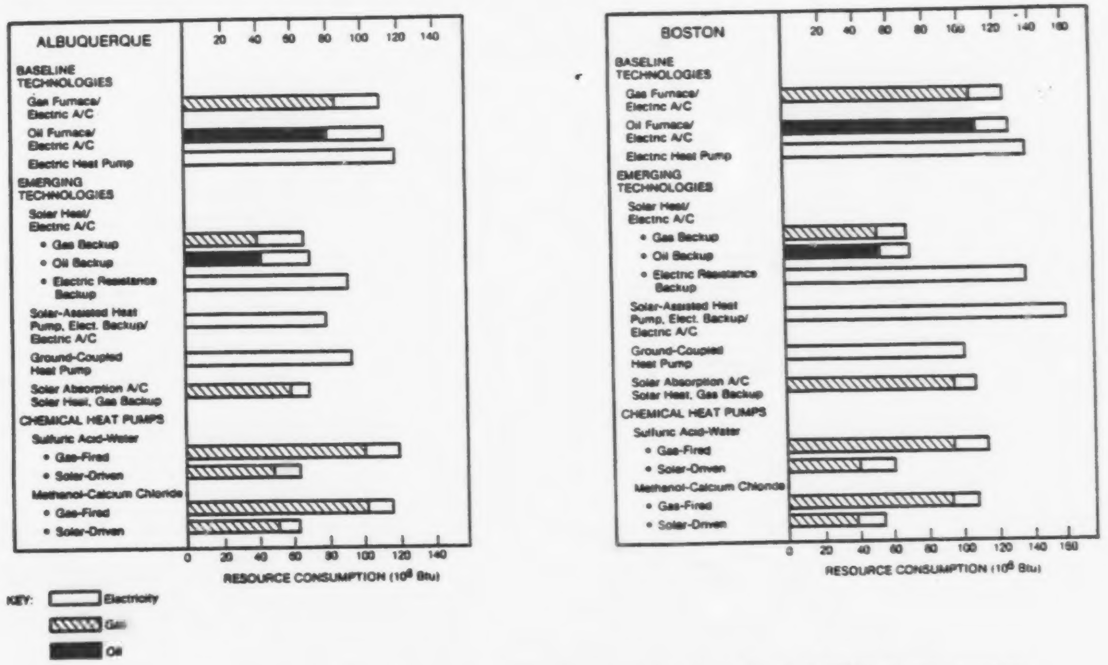


Figure 1. Annual Energy Resource Consumption for Residential HVAC Technologies

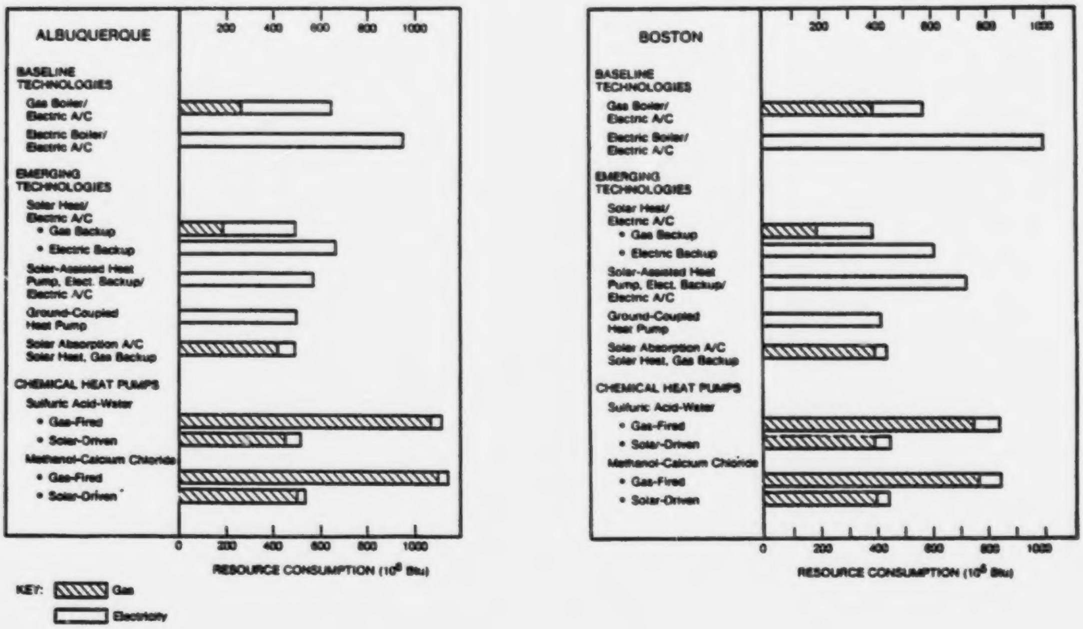


Figure 2. Annual Energy Resource Consumption for Commercial HVAC Technologies

- The TRW estimate of the cost-effectiveness of CHP systems in HVAC applications, using constant-dollar annual levelized cost as the criterion, shows that both the methanolated-salt and sulfuric acid systems can be competitive with baseline and emerging technologies in specific applications and locations. In residential applications, the gas-fired methanolated-salt system (EIC) is comparable to baseline technologies and is clearly more cost-effective than emerging systems, independent of location. The residential solar-driven methanolated-salt CHP is cost-competitive in the Southwest (Albuquerque) but not in the Northeast (Boston). In general, the solar-driven commercial CHP systems are more expensive to own and operate than all baseline systems and most emerging systems. The gas-fired commercial CHP systems are less expensive than the solar-driven CHP systems, but remain more expensive than the baseline and emerging technologies. The levelized annual cost of owning and operating both CHPs and competing systems is illustrated by Figure 3 for residential systems and Figure 4 for commercial systems.

- Both CHP concepts (methanolated salt and sulfuric acid) were evaluated based on performance data supplied by their respective developers. Each is technically able to operate in the industrial process-heat temperature range and there is no severe technical limitation which would preclude the use of either CHP for industrial waste heat recovery and upgrading. Both the sulfuric acid and methanolated salt systems would consume about the same amount of ancillary energy (electricity) during operation. The higher capital cost of the sulfuric acid system makes it apparently more expensive to own and operate, relative to the methanolated salt system. The capital cost of the methanol system is less well-developed than that for the sulfuric acid system. It is quite possible that a more detailed evaluation of the EIC system, equivalent to that done by Rocket Research for the sulfuric acid system, would indicate a higher real capital cost and would eliminate the apparent cost advantage of the methanolated salt system. The EIC system is being developed for space conditioning applications and has never been specifically configured for waste-heat upgrading. It has the disadvantage of a very large system envelope in the industrial applications, with 360 cubic feet of calcium chloride salt bed required for a one-million Btu/hr process water reheating (from 240°F to 260°F) case, and over 1400 cubic feet required for a one-million Btu/hr process steam (300°F, 67 psia) case. The methanolated salt system is evaluated for the process reheating case, but is considered impractical at its current stage of development for the process steam application.

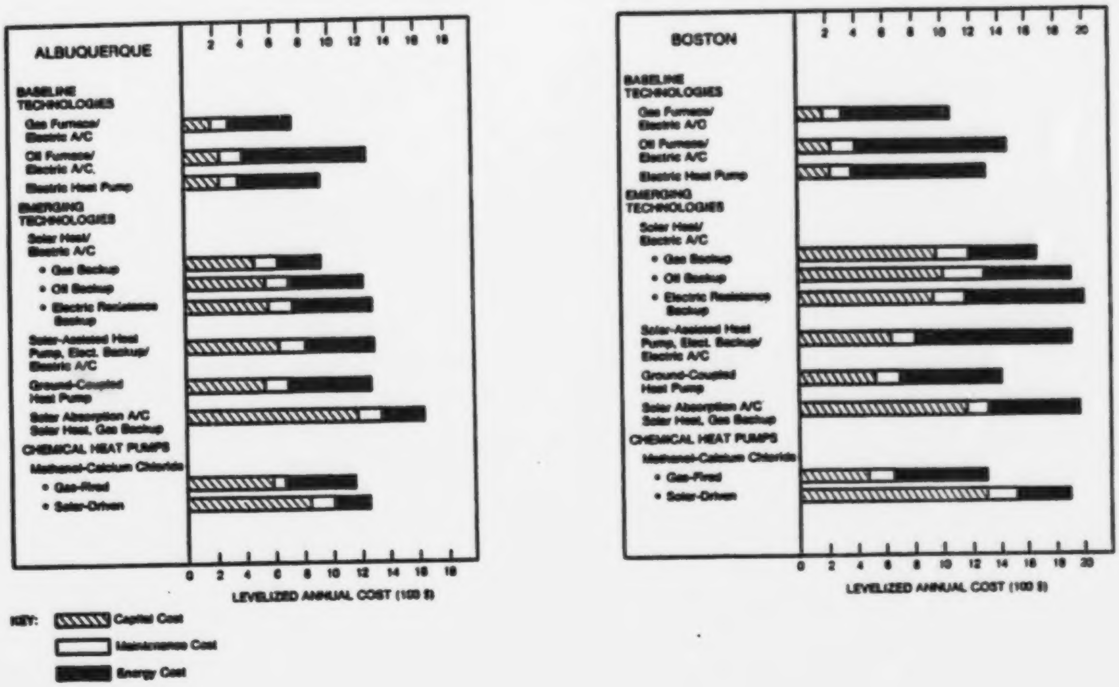


Figure 3. Levelized Annual Cost of Owning and Operating Residential HVAC Technologies

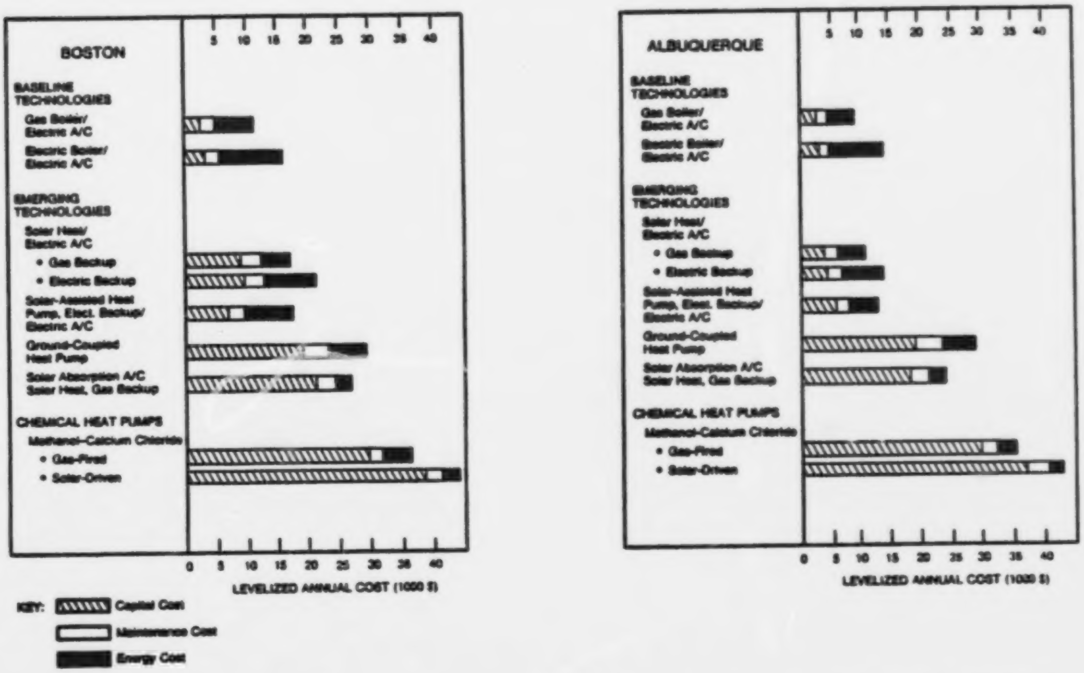
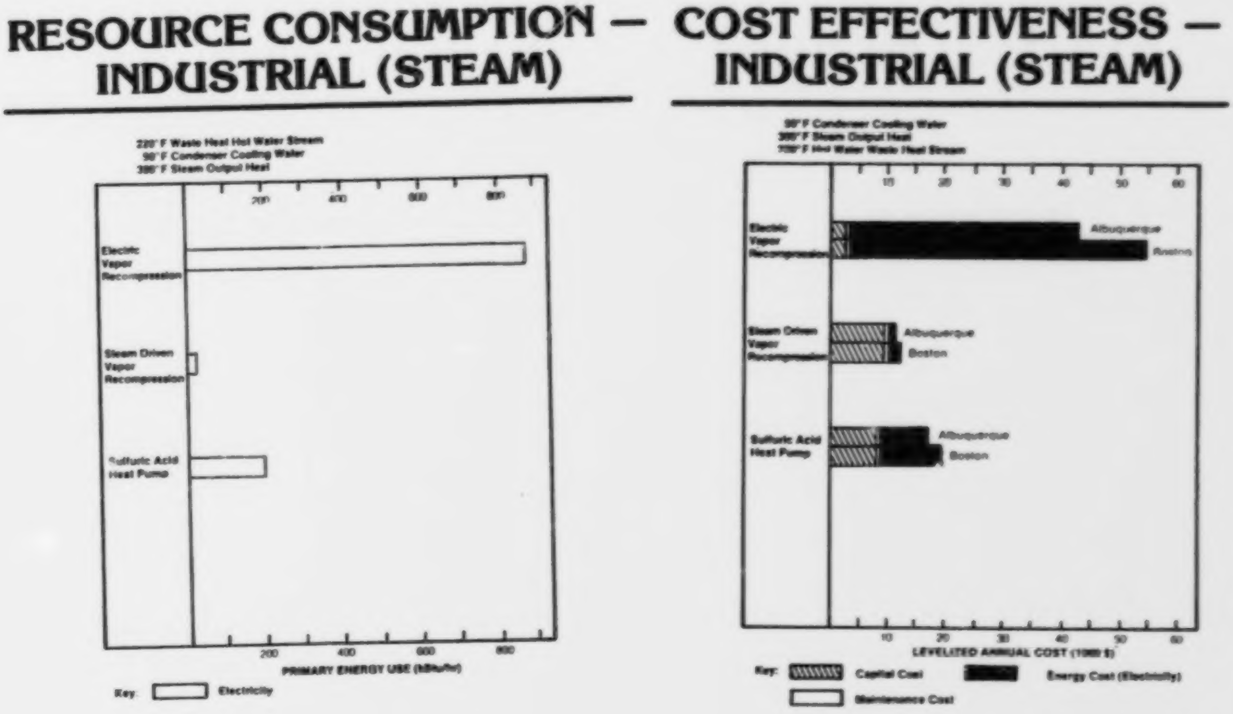


Figure 4. Levelized Annual Cost of Owning and Operating Commercial HVAC Technologies

- Use of the sulfuric acid CHP for industrial waste heat recovery from a 220°F, 67 psia process steam could be competitive with both baseline and emerging systems. Compared to a baseline system consisting of steam raised directly in a fuel-fired boiler, the CHP is both cost-effective and conservative of energy resources. The individual CHPs were also found to be much more energy conservative than an electrically-driven vapor recompression system. A vapor-driven vapor-recompression system was the most energy-conservative system evaluated, although the practical application of a steam-driven turbine exhausting to very low pressure could reduce the energy efficiency of the system. The concept of vapor recompression is used commercially to conserve energy in evaporation and distillation operations. The concept has been specifically adapted to the industrial waste heat recovery application and, although there is no known commercial system in such an application, the engineering basis is considered valid. The annual consumption of energy resources and levelized annual cost of owning and operating the sulfuric acid CHP and its competitors in the process steam application are illustrated in Figure 5.


RESOURCE CONSUMPTION — INDUSTRIAL (STEAM)

COST EFFECTIVENESS — INDUSTRIAL (STEAM)

Figure 5. Energy Resource Consumption and Levelized Annual Cost for Several Industrial Heat Pumps Used for Raising 1.0 MBtu/hr of Process Steam

- The use of either CHP for industrial waste heat recovery from a 210°F waste stream to reheat a process steam from 240°F to 260°F could be competitive with both baseline and emerging systems. Compared to a baseline system consisting of steam raised directly in a fuel-fired boiler, the CHP are both cost-effective and conservative of energy resources. The industrial CHPs were also found to be much more energy conservative than an electrically-driven vapor recompression system. A vapor-driven vapor-recompression system was the most energy-conservative system evaluated, although the practical application of a steam-driven turbine exhausting to very low pressure could reduce the energy efficiency of the system. The annual consumption of energy resources and levelized annual cost of owning and operating both industrial CHP's and their competitors in the process water reheating application are illustrated in Figure 6.

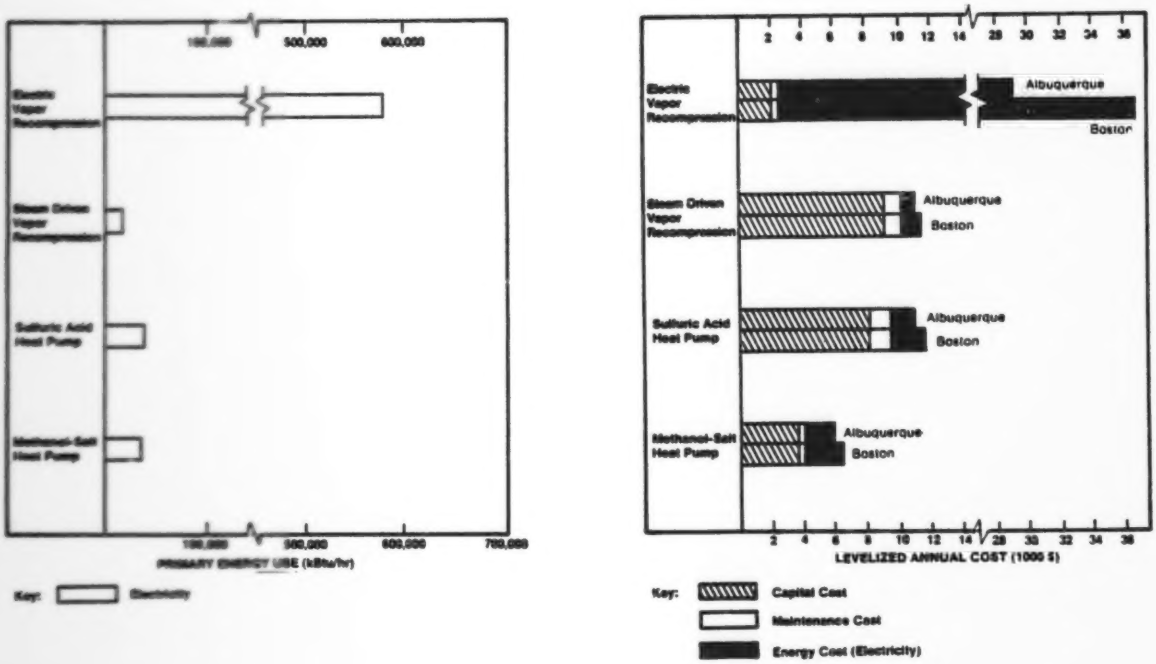


Figure 6. Energy Resource Consumption and Levelized Annual Cost for Several Industrial Heat Pumps Used to Provide 1.0 MBtu/hr for Process Water Reheating (240°-260°F)

PUBLICATIONS/REPORTS

The final technical report for this project is complete and will be available through NTIS.

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2. E. C. Clark and D. K. Carlson, "Development Status and Utility of the Sulfuric Acid Chemical Heat Pump/Chemical Energy Storage System." AIAA Paper 809182. Proceedings of the 15th Inter-Society Energy Conversion Engineering Conference, August 18-22, 1980.

3. P. O'D. Offenhartz, "Methanol-Based Heat Pump for Solar Heating, Cooling, and Storage. Phase II." Draft Final Report EIC Corporation, October 1979. U.S. DOE under Contract to Sandia Laboratories #18,8423.

4. R. Gorman and P. Moritz, "Hydride Heat Pump, Volumes I and II." TRW Energy Systems Planning Division, McLean, Virginia, for Argonne National Laboratory, May 12, 1978.

PROJECT SUMMARY

Project Title: Metal Hydride/Chemical Heat Pump Development Project

Principal Investigator: Samuel J. Cunningham

Organizations:

Southern California Gas Company (prime)
810 So. Flower Street
Los Angeles, CA 90017

Solar Turbines Incorporated (subcontractor)
2200 Pacific Highway
San Diego, CA 92138

Project Goals: Develop cost effective metal hydride/chemical heat pump for residential, commercial or industrial applications. The specific goal of Phase I is to identify the target application of the heat pump and detail design of the evaluation unit to be built in Phase II. An advance prototype unit will also be designed in Phase II, and built and tested in Phase III.

Project Status: The Southern California Gas Company is currently under contract to proceed with Phase I of the program identified above. Funding for Phase II and III are not yet obligated. The conceptual design and market survey have been completed. Potential applications have been identified and characterized. Competing systems have also been characterized in each potential application. A screening criteria was developed to evaluate the MHHP for each potential application. This led to a recommended application for the MHHP as an industrial temperature upgrader. Efforts to develop the thermal and mechanical designs, controls systems, and selected hydride materials are underway. Heat transfer enhancement and high COP are goals of the technical work. Development of detailed design will be completed in Phase I.

In Phase II, the EDTU will be fabricated, tested, rebuilt as necessary and retested. This will lead to the detailed design of an Engineering Evaluation Test Unit (EETU). Additionally, based on the technical results obtained in this Phase, a more indepth commercial feasibility analysis will be performed. During Phase III, the EETU will be fabricated and tested.

Contract Number: 530498-S

Contract Period: February 1, 1981 through March 30, 1984

Funding Level:

Phase I - $250,000 committed
Entire Project - $881,822

Funding Source: Brookhaven National Laboratory

METAL HYDRIDE/CHEMICAL HEAT PUMP DEVELOPMENT PROJECT

Hector A. Madariaga
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810 South Flower Street
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and

David A. Rohy
Solar Turbines Inc.
2200 Pacific Highway
San Diego, California 92138

ABSTRACT

A metal hydride heat pump (MHHP) is a chemical heat pump containing two different hydrides and using hydrogen as a working fluid for the storage and/or recovery of thermal energy. It utilizes the heat of reaction of hydrogen with specific metal alloys. The MHHP design can be tailored to provide heating and cooling or temperature upgrading over a wide range of input and ambient temperatures. This system can be used with a variety of heat sources including industrial waste heat, solar energy or a fossil fuel. Temperatures as low as 130°F can drive the MHHP when a suitable sink is provided. A project is currently underway to develop this unique heat pump for a specific application.

The goals of the project include the development of cost effective hydride containers with high heat transfer and low mass; design and fabrication of a laboratory evaluation model; and design and fabrication of a demonstration unit. Extensive component and system test will provide the data for the design processes.

INTRODUCTION

A unique chemical heat pump is being developed in a project sponsored by the Brookhaven National Laboratory. The main contractor, Southern California Gas Company has selected Solar Turbines Inc. of San Diego as a technical subcontractor and Booz, Allen and Hamilton, Inc. of Bethesda, Maryland for its marketing and commercialization expertise. [Booz, Allen and Hamilton, Inc. is fully funded by Southern California Gas Company and receives no government funds for their participation in this project (Fig. 1)]. The three-phase effort is scheduled for completion in March of 1984.

At the start of Phase I, the conceptual design was established followed by a national market survey and characterization to identify the most attractive applications and markets. This is being followed by a firstcut commercial feasibility analysis. Upon the completion of these tasks, an Engineering Development Test Unit (EDTU) will be designed for the target market application.

In Phase II, the EDTU will be fabricated, tested, rebuilt as necessary and retested. This will lead to the detailed design of an Engineering Evaluation Test Unit (EETU). Additionally, based on the technical results obtained in this phase, a more in-depth commercial feasibility analysis will be performed. During Phase III, the EETU will be fabricated and tested.

The Southern California Gas Company is currently under contract to proceed with Phase I of the program identified above. Funding for Phases II and III are not yet obligated. The conceptual design and market survey have been completed. Potential applications have been identified and characterized. Competing systems have also been characterized in each potential application. A screening criteria was developed to evaluate the MHHP for each potential application. This led to the recommended application for the MHHP as an industrial temperature upgrader. Efforts to develop the thermal and mechanical designs, controls systems, and selected hydride materials are underway. Heat transfer enhancement and high COP are goals of the technical work. Development of detailed designs will complete Phase I.

HEAT PUMP CONCEPT

The metal hydride heat pump (MHHP) consists of two different metal alloys that absorb and desorb hydrogen. Heat is generated on H_2 absorption while H_2 desorption is endothermic. The two metals are maintained in separate parts (Fig. 2) of the same container. The hydrogen is thermally driven from hydride 1 to hydride 2 and back. Hydrogen is not consumed. Because the cooling processes are intermittent, two or more containers are used in an out-of-phase manner to achieve continuous cooling or temperature upgrading. Heat amplification is nearly continuous.

The charge and refrigeration side of the heat pump cycle are shown in Figure 2. In that figure hydrogen is driven from the warm side alloy to the cold side alloy. Heat generated in the cold side alloy by H_2 absorption is rejected by the nearly ambient temperature water, T_C. Once the tube is charged (all the hydrogen is on the cold side), the outside temperatures are changed reversing the pressure differential inside the tube. The hydrogen then returns to the warm side hydride. To provide the heat of dissociation the cold side alloy extracts heat from the cooling fluid at T_E. Ambient temperature water is sufficient to maintain the warm side hydride at a low enough temperature to remove

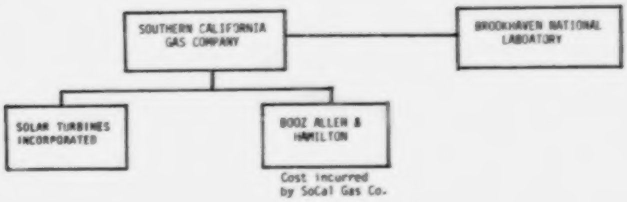
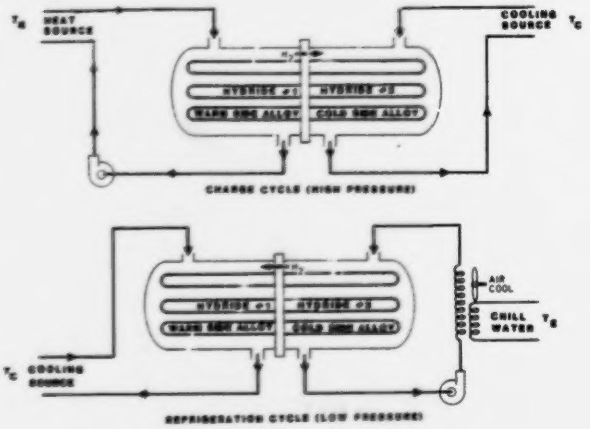

SOUTHERN CALIFORNIA GAS COMPANY
BROOKHAVEN NATIONAL LABORATORY
SOLAR TURBINES INCORPORATED
BOOZ ALLEN & HAMILTON
Cost incurred by SoCal Gas Co.

Fig. 1. Project Organization

the heat of formation while it reabsorbes the H_2. Once all the hydrogen is on the warm side hydride recharging must occur. Heating and temperature upgrading work in similar fashions but extract useful at different temperatures.



T_G = 180°F OR HIGHER, T_C = 80-100°F, T_E = 35°F OR LOWER

Fig. 2. Heat Pump Conceptual Design

The maximum possible COP of cooling is nearly one, while the maximum COP of heating is two. COP calculation methods vary. The numbers shown here are based on thermal input compared with thermal output. Since this cycle can operate from very low temperature sources, the economic value of the input energy can be very low. The COP numbers have little dependence on the size of the unit. Thus, the MHHP which is almost silent in operation, could prove to be extremely efficient and economic for small scale (0.5 to 10.0 tons of refrigeration) units. Another unique application is for vehicle air conditioning. Those units would be driven by the thermal energy in the cooling fluid and require no shaft horsepower.

MARKET SURVEY AND APPLICATION SELECTION

An extensive market survey has been undertaken as part of this effort. Only the highlights are reported here. This task involved characterization of the marketplace for HVAC equipment, definition of configurations for the MHHP in the market, selection of screening criteria, and finally, selection of a target application for this effort. A preliminary commercialization plan is being developed.

Characterization of Major Markets

Based upon telephone conversations and personal interviews with HVAC manufacturers and other HVAC industry participants, Booz-Allen completed characterization of the residential, commercial, and industrial markets. The characterization included: (1) heating and cooling equipment shipments, based upon industry trade association data and DOE estimates; (2) air conditioning shipments, by both end-use application and cooling capacity; (3) projections of future market growth, new starts and replacement markets for the residential sector, square footage for commercial buildings, and energy use in each of five temperature regimes, for the industrial sector; (4) breakdown of fuel use for new types of HVAC equipment and industrial heat recovery equipment.

Definition of Configurations for the MHHP

As a result of the market study, configurations were selected for the residential, commercial, industrial and transportation sectors (Fig. 3). For each of the configurations, Booz-Allen has identified a set of candidate applications. For example, for the heat amplifier in the industrial sector, Booz-Allen identified eight industrial processes in which the heat amplifier is technically feasible.

Selection of Screening Criteria

A set of criteria was developed to evaluate each MHHP configuration on a comparative basis. Each criterion was weighted to provide its relative importance. (The weighting is a consensus of the team members.) This is shown in Figure 4.

Selection of MHHP Configuration

Once the criteria were selected and weighted, the team members selected the one configuration to be pursued technically in this program. Configurations were ranked according to the following steps: (1) Assign weighting factors to each of the screening criteria. (2) Rank score each configuration for

TECHNICAL (40%)		MARKET (50%)		OTHER (10%)	
. SIZE, WEIGHT	(5.5%)	. POTENTIAL IN 1985-1990	(5.5%)	. TAX CREDIT APPLICABILITY	(2.0%)
. SAFETY	(5.0%)	. ADDRESSABLE SIZE	(7.5%)	. NOISE	(3.5%)
. CAPACITY - THERMAL	(6.0%)	. ADAPTABILITY TO TDS	(7.5%)	. COMPT. TECHNOLOGY ADVANTAGES/DISADVANTAGES	(4.5%)
. TEMPERATURE RANGE	(8.0%)	. MAXIMUM FACTORY COST	(16.5%)		
. COMPET. TECHNOLOGY STATUS	(8.5%)	. COMPETING TECHNOLOGY ECONOMICS	(13.0%)		
. DEVELOPMENT RISK	(7.0%)				

Fig. 4. Weighting Factors of the Evaluation Criteria

each screening criteria. (3) Calculate a weighted average score for each configuration. (4) Conduct one final screen of highly ranked configurations. (5) Choose the one configuration which fits all requirements.

The results of this extensive market survey show that the most promising MHHP configuration is the industrial waste heat driven temperature upgrade cycle. This cycle uses an intermediate temperature heat source and provides a higher temperature process stream. One of the critical factors in this decision was the amount of waste heat that is available in industrial processes. Applications in the food, textile, pulp and paper and chemical industries appear very promising.

RESIDENTIAL SECTOR	COMMERCIAL SECTOR	INDUSTRIAL SECTOR	TRANSPORTATION SECTOR
• HEATING ONLY UNIT	• PACKAGED, FUEL-FIRED UNITARY HEATING/COOLING UNIT	• HEAT AMPLIFIER (FUEL-DRIVEN)	• TRUCK/TRACTOR CAB AIR CONDITIONER
• FUEL-FIRED HEATING/COOLING	• SAME BUT WITH ELECTRIC COOLING	• TEMPERATURE AMPLIFIER (WASTE HEAT-DRIVEN)	• "REEFER SHIP" REFRIGERATION
• SOLAR-ASSISTED (LOW GRADE) HEATING ONLY	• PACKAGED SOLAR-DRIVEN HEATING/COOLING	• REFRIGERATION UNIT	• TRUCK TRAILER REFRIGERATION
• SOLAR-DRIVEN HEATING OR HEATING/COOLING	• FUEL-DRIVEN HEATING ONLY UNIT (BOILER SUBSTITUTE)		

Fig. 3. Candidate Product Configuration

MATERIALS

The hydride materials used in the MHHP must have several important characteristics. First they must absorb and desorb hydrogen near the three operating temperatures of the MHHP, T_G, T_C and T_E. Second, the absorption-desorption PCT (pressure, composition, temperature) curves must have broad plateaus (Fig. 5) and low hysteresis. The flat (constant pressure) plateaus allow the hydrogen to transfer within the MHHP at constant temperature and pressure. A family of PCT curves for one alloy provide data for van't Hoff curves and heats of formation. The quantity of hydrogen absorbed per mole of metal, long-term chemical stability and susceptibility to poisoning are other characteristics sought when selecting the appropriate alloys for an MHHP. Alloys exist or can be tailored for almost any temperature, but little of the required data is known for every alloy. In the current project alloys are selected using all known data. Only those data absolutely required for the selected application will be generated, since significant time is required for the tests.

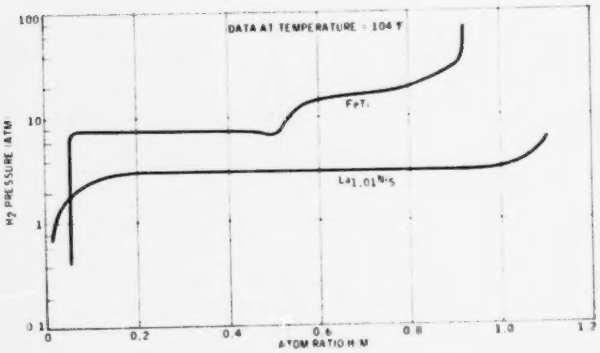


Fig. 5. Plateau Pressure as a Function of Hydrogen Content

The MHHP requires two different hydrides to work in tandem, one alloy operating on the cold side and the other operating on the warm side. The plateau pressures must be such that the hydrogen will be driven between the two alloys. Naturally, the hysteresis between the absorption and desorption plateau pressures will be an important factor in selection of the MHHP temperature-pressure cycle. The hysteresis tends to lower the maximum ΔT at which the MHHP can operate.

Three alloy pairs have been selected as examples applicable to a temperature upgrade MHHP application. The operating temperature ranges were chosen to be T_E (low temperature) 20-36°C (68-97°F), T_C (mid temperature) 50-96°C (122-192°F) and T_G (high temperature) 140-180°C (284-356°F). The heat pump would therefore upgrade heat from T_C to T_G, given a range of 40-130°C increase

Three alloy pairs were selected on the basis of the van't Hoff curves:

	Cold Side	Warm Side
1.	$LaNi_5$	$LaNi_{4.6}Al_{0.4}$
2.	$LaNi_5$	$LaNi_{4.5}Al_{0.5}$
3.	$MmNi_{4.15}Fe_{0.85}$	$LaNi_5$

The second combination shows promise in the MMHP temperature upgrade application where as the other two do not appear acceptable because of hysteresis.

The heat of formation of a metal hydride is relatively independent of temperature, allowing the mid-plateau pressure/temperature relationships to be presented on a van't Hoff diagram (where the logarithm of the pressure is given versus the inverse of the temperature). Figure 6 is an illustration of a van't Hoff plot of several metal hydride alloys. The information can be conveniently displayed in analytical form by giving the equation of the straight line. This equation can take the form

$$RT\, \ell n \Delta P = \Delta H + \Delta T\, \Delta S \quad \underline{\text{or}} \quad \Delta P = A \exp[-B/T]$$

where ΔH is the enthalpy of formation, ΔS is the change in entropy and A and B are constants in pressure and degrees absolute respectively. This allows the calculation of the mid-plateau pressure at any reasonable temperature. In addition, only a few experimental points are necessary to extrapolate the data to other temperatures.

The fundamental representation of the absorption-desorption hysteresis parameter is $\ell n(P_a/P_b)$ as suggested by Lundin and Lynch (Ref. 1). This ratio remains fairly constant over a wide range of temperatures. This provides a means of approximating the absorption pressure when several desorption data and absorption data for one condition is known.

Using these analytical representations of the plateau pressure and the hysteresis, pressure and temperature plots of the alloy pairs over the appropriate temperature range were generated for each alloy pair considered.

The hydride alloy pair $LaNi_5/LaNi_{4.5}Al_{0.5}$ is an example of a combination that would operate in the specified temperature ranges. The van't Hoff parameters used were $Lani_5$: $A = 4.25 \times 10^5$ atm. and $B = 3712$ K (taken from Ref. 2) and $LaNi_{4.5}Al_{0.5}$: $A = 5.97 \times 10^5$ atm. and $B = 4580$ K (taken from Ref. 3). The hysteresis parameter for $LaNi_5$ was 0.19 but due to a large difference in the reported values for $LaNi_{4.5}Al_{0.5}$, the calculations were performed twice using 0.08 (Ref. 3) and 0.52 (Ref. 4) with the results being shown in Figures 7 and 8 respectively. Even with the large variations in values for the hysteresis, the cycle will operate under either condition. As the hysteresis of the warm side alloy increases, the maximum upgrade temperature decreases. This is illustrated in the example P-T cycles, i.e., lowering T_G from 162°C to 144°C.

All possible alloy pairs will require this type of analysis, unfortunately, not all alloys are sufficiently characterized to allow this to be done. In addition, inconsistencies in the data can lead to inconclusive results. Further alloy characterization will be necessary on any promising alloy pair to confirm design parameters and attractive alloys that are missing pertinent data must also be more fully characterized.

THERMAL MECHANICAL DESIGN

Hydride materials comminute and expand about 25 percent by volume upon hydriding. These characteristics make heat transfer and physical containment difficult. A primary goal of the program is to design containment vessels with low mass and high heat transfer. In addition a separator (filter) must be designed into the container to separate the metal powders from the hydrogen gas. These separators cannot operate by capturing particles or they soon cause high pressure drops and stop the MHHP. High thermal transfer rates are difficult with powders but essential if the MHHP is to achieve cost goals. The higher the transfer rate, the less powder is required per ton of refrigeration.

A computer program developed by Solar Turbines Incorporated (STI) some years ago is utilized to study the heat transfer and thermal transient problems of various MHHP heat exchanger configurations. This program uses nodal analysis and presents solutions in terms of temperature versus time information. Analysis of various hydride heat exchanger configurations has been started. Tubular approaches under study are shown in Figure 9.

A parametric study of other geometries, such as an externally finned tube hydride heat exchanger is being conducted to determine concept feasibility and optimum design geometry. The finite element heat

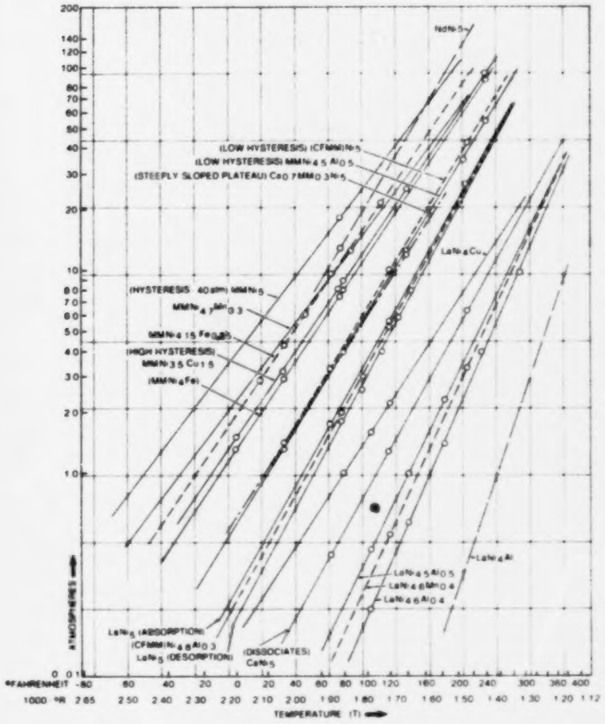


Fig. 6. Pressure/Temperature Relationships at Mid-Plateau

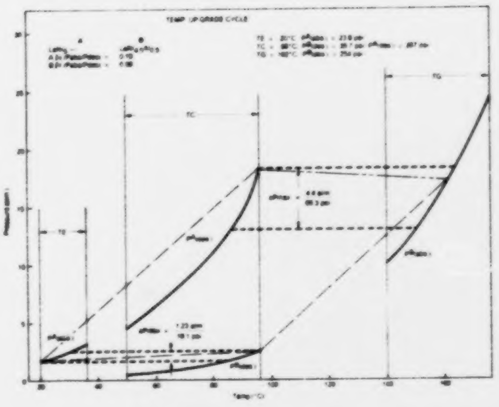


Fig. 7. Pressure/Temperature Up-Grade Cycle With Low Hysteresis

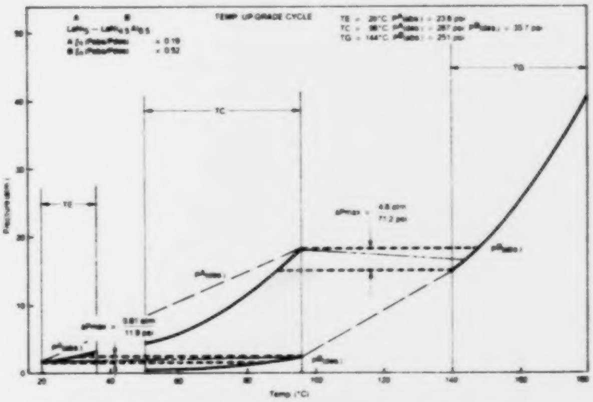


Fig. 8. Pressure/Temperature Up-Grade Cycle With High Hysteresis

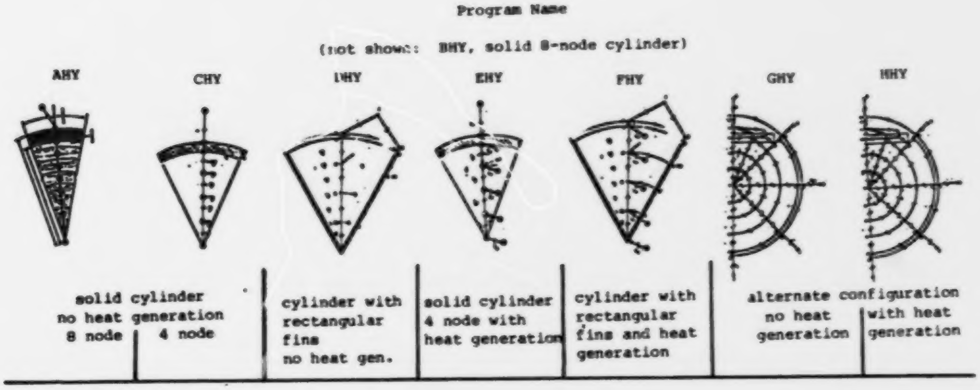
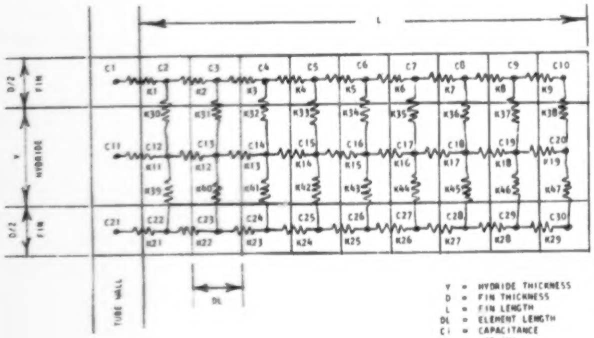

Program Name
(not shown: BHY, solid 8-node cylinder)
AHY
CHY
DHY
EHY
FHY
GHY
HHY
solid cylinder
no heat generation
8 node
4 node
cylinder with
rectangular
fins
no heat gen.
solid cylinder
4 node with
heat generation
cylinder with
rectangular
fins and heat
generation
alternate configuration
no heat
generation
with heat
generation

Fig. 9. MHHP Tubular Heat Exchanger Configuration

transfer analysis program evaluates the effect of dimension changes on the performance of this system. The basic heat exchanger model is a tube with annular fins. The working fluid flows through the tube and the hydride is packed between the fins. Figure 10 shows the basic finite element model used in this analysis. The three left most nodes are located in the tube wall. The upper and lower rows of remaining nodes are located within the fins. All other nodes are located within the hydride powder. Figure 11 shows preliminary analysis of this design approach. Plotted is the time to reach 90 percent of the temperature difference versus hydride thickness (fin thickness is a parameter).


L
D/2
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HYDRIDE
TUBE WALL
DL
C1
C2
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Y = HYDRIDE THICKNESS
D = FIN THICKNESS
L = FIN LENGTH
DL = ELEMENT LENGTH
Ci = CAPACITANCE
= ρiCpiVi
Ki = CONDUCTANCE
= kiAi/li

Fig. 10. Finned Tube Hydride Heat Exchanger

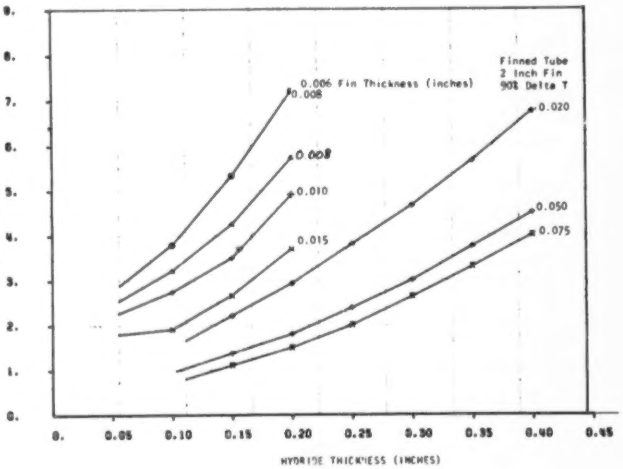

Fig. 11. Preliminary Analysis of Design Approach

A test rig to study the actual heat transfer characteristics of computer selected heat exchanger structures is being built. This rig will be used to verify and support the results of the computer studies.

A filter test rig has been fabricated to determine the pressure drop across various hydride powder/filter configurations. Previous filter testing has indicated that the pressure drop across a specific filter can vary substantially depending upon the orientation of the filter in relation to the metal hydride powder. The test assembly can be mounted in any atitude and any amount of hydride powder can be packed between the filters. Materials used to stratify the hydride powders such as aluminum foam, can also be inserted between the filters. Both flat and tubular filters will be tested.

CONTROLS

Controls for the MHHP will be very simple once the timing cycles are well documented and the strategies developed. For the Phase II unit now under development, the control unit must allow for control strategy flexibility and provide for extensive data acquisition.

The following list of capabilities define what the control unit must provide to do an effective job. (1) Maintain a setpoint temperature for a given space. (2) Establish a flow circulation path for heating and cooling fluids. (3) Maintain rate of flow for heating and cooling flows. (4) Optimize heating and cooling cycles for maximum efficiency. (5) Display status and measured values on the system that indicates performance of the system (this will be limited on production system. (6) Maintain surveillance of key system parameters. Check for out-of-tolerance operation. If a condition exists which could produce harmful results take corrective action or effect a gradual shutdown.

The hardware prototype control unit will be built utilizing the Intel "Multi Bus™" and catalog circuits compatible to that bus system. Little or no hardware development is anticipated. For Phase III the control will be accomplished with a single chip microcomputer.

CONCLUSIONS

Metal hydrides are used to provide heating, cooling or temperature upgrading in the low temperature (130 to 400°F) regime. Various heat sources can be utilized. In the current effort, heat upgrading for industrial processes will be pursued. Waste heat will drive the system. Technical work is concentrated on material selection, development of hydride containers with high thermal conductivity and low mass, and on the control scheme. Detailed designs will be provided in Phase I for the laboratory model to be fabricated in Phase II.

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3. M. H. Mendelsohn, D. M. Gruen and A.E. Dwight, The Effects of Aluminum Additions on the Structural and Hydrogen Absorption Properties of AB_5 Alloys With Particular Reference to the $LaNi_{5-x}Al_x$ Ternary Alloy Systems, J. Less Common Metals, 63 (1979), pp. 193-207.

4. H. Diaz, A. Percheron-Gnegan, J. C. Achard, C. Chatillon and J. C. Mathieu, Thermodynamic and Structural Properties of $LaNi_{5-y}Al_y$ Compounds and Their Related Hydrides, Int. J. Hydrogen Energy, 4, pp. 445-454 (1979). [Also 2nd World Hydrogen Energy Conference, 1978, p. 2653.]

PROJECT SUMMARY

Project Title: Metal-Hydride Heat-Pump Development

Principal Investigators: H.I. Abelson and J.M. Clinch

Organization: Center for Electrochemical Technology
Argonne National Laboratory (ANL)
9700 South Cass Avenue
Argonne, IL 60439

Project Goals: Provide technical assistance to Brookhaven National Laboratory (BNL) in monitoring the development of the metal-hydride heat-pump contract work. Carry out, in support of the project, performance and cost analyses of such a heat pump.

Project Status: The analytical work associated with developing general expressions for the system coefficient of performance (COP) in the heating and cooling modes, as applied to a multi-tube metal-hydride heat pump with regenerative stages, has been completed. The system thermodynamics and the derivation of the COP are described in detail in the July/August 1981 issue of the AIAA Journal of Energy. Theoretical upper bounds on the COP have been established, and the sensitivity of the heating COP to various key system parameters has been investigated. Periodic progress reports in connection with the metal-hydride heat-pump contract have been reviewed and evaluated.

Contract No: AL 10-05-10-5/ANL 49405

Contract Period: October 1, 1980 through September 30, 1981

Funding Level: $100,000 BA/BO

Funding Source: Brookhaven National Laboratory

METAL-HYDRIDE HEAT-PUMP PERFORMANCE STUDIES

H.I Abelson and J.M. Clinch
Argonne National Laboratory
Argonne, Illinois

ABSTRACT

We have developed expressions for the coefficient of performance (COP) for both heating and cooling by a multi-tube, metal-hydride heat pump that employs regenerative heat exchange. We have established theoretical upper bounds on the COP and determined the sensitivity of the heating COP to variations in key system parameters. We also have estimated the COP for a baseline design and explored potential design improvements.

INTRODUCTION

Recent ANL efforts in metal-hydride heat-pump development have focused on analytical predictions of thermal performance for a multi-tube unit. The ANL multi-tube design uses many identical sealed tubes, each containing (at opposite ends) a high-temperature and a low-temperature hydride. To minimize performance losses from thermal cycling, the unit employs regenerative heat exchange. The multi-tube heat pump was described at last year's Annual Contractors Review.(1) Results of a thermodynamic analysis of this unit, including expressions for the coefficient of performance (COP) for both the heating and cooling modes and specific-design COP estimates, have been published recently.(2)

This year, activities have centered on analysis of system design and operating parameters and determination of the sensitivity of thermal performance to variations in these parameters. We have sought methods of improving the system COP and identified areas for future development efforts.

SYSTEM DESCRIPTION

The key element in the proposed design is a sealed tube containing a different hydride bed at each end (see Fig. 1). Filter material in the central portion of the tube permits hydrogen flow between beds while preventing carry-over of hydride powder. The central portion also retards the conduction of heat between the two ends. Because of the inherently low conductivity of hydride powder, heat transfer between each bed and the fluid medium surrounding the sealed tube must be enhanced.

Tubes are combined within a cylindrical shell to form a bundle (see Fig. 2). A central tube-sheet separates the high-temperature (A) and low-temperature (B) ends of the bundle, and each end is divided in half axially by a baffle. Fluid enters the face of each bundle-end, flows axially over the tubes above the baffle, reverses direction to flow over the lower tubes, and exits by the same face. Bundles are arranged in a circular pattern within a housing to form the main body of the heat pump. The ends of each bundle progressively undergo the thermodynamic cycle described in Ref. 2. For analysis, we assume that every tube contained within the same bundle is in the same state at any instant of time, and that thermal gradients within the tubes are negligible. Thus, at any time, the temperature of each bundle-end (exclusive of the contained fluid) is given by a single value.

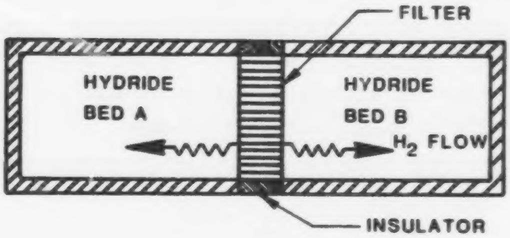

Fig. 1 Schematic Diagram of Hydride Tube

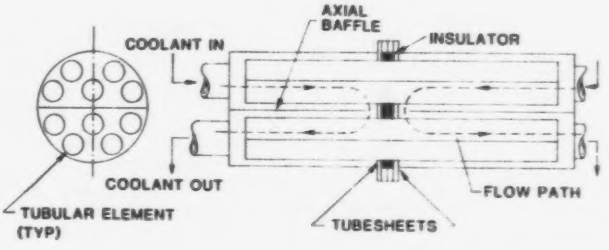

Fig. 2 Construction of Representative Tube Bundle

The cycling of each bundle is accomplished using a multiport rotating valve at each end of the unit. These valves, rotating at constant speed, connect each stationary bundle with the appropriate fluid loop as the bundles progress through the cycle. One revolution of the valve causes each bundle to undergo a complete, identical cycle.

Figure 3 shows multi-tube heat-pump operation for a 24-bundle unit. The B end should be viewed as if one were looking "through" end A. For example, the bundles marked ▼ at the B end are the same as those marked ▽ at the A end. The valves rotate at constant speed, so the time each bundle spends executing a given process is proportional to the number of valve positions allocated to that process.

COEFFICIENT OF PERFORMANCE

We have derived expressions for the COP$^{(2)}$ for both the heating and cooling modes by applying its basic definition (i.e., the ratio of the "energy sought" to the "energy that costs") over a complete cycle. Here, the "energy that costs" is taken to be the total energy input from the high-temperature source, not including parasitic power requirements. The COPs for the heating and cooling modes, respectively, are given by:

$$\mathrm{COP}_h = \frac{\frac{1}{2} f_A(\Delta H/M)_A(\Phi_{A_a} + \Phi_{B_a}) + \dfrac{Z + \rho_A C_A}{\rho_A}(1-\varepsilon_A)(T_H - T_{i_A})}{\frac{1}{2} f_A(\Delta H/M)_A \Phi_{A_d} + \dfrac{Z + \rho_A C_A}{\rho_A}(1-\varepsilon_A)(T_H - T_{i_A}) + \dfrac{f_A(\Delta H/M)_A}{f_B(\Delta H/M)_B}\,\dfrac{Z + \rho_B C_B}{\rho_B}(1-\varepsilon_B)(T_{i_B} - T_L)} \tag{1}$$

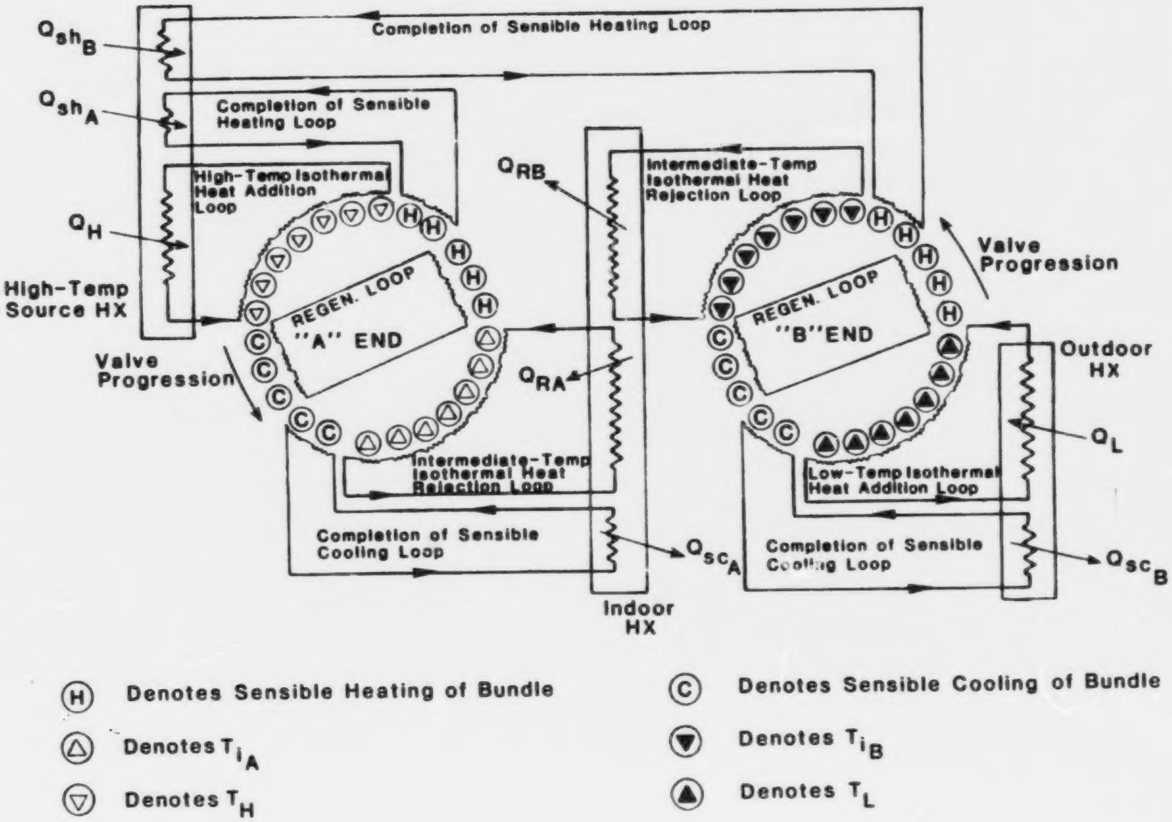
Q_{sh_B}
Completion of Sensible Heating Loop
Q_{sh_A}
Completion of Sensible Heating Loop
High-Temp Isothermal Heat Addition Loop
Q_H
High-Temp Source HX
Valve Progression
REGEN. LOOP
"A" END
Q_{RB}
Intermediate-Temp Isothermal Heat Rejection Loop
Q_{RA}
Intermediate-Temp Isothermal Heat Rejection Loop
Completion of Sensible Cooling Loop
Q_{sc_A}
Indoor HX
REGEN. LOOP
"B" END
Valve Progression
Outdoor HX
Q_L
Low-Temp Isothermal Heat Addition Loop
Completion of Sensible Cooling Loop
Q_{sc_B}
H
C
Ⓗ Denotes Sensible Heating of Bundle
Ⓒ Denotes Sensible Cooling of Bundle
△ Denotes T_{i_A}
▼ Denotes T_{i_B}
▽ Denotes T_H
▲ Denotes T_L

Fig. 3 Schematic Representation of Operation of a Multi-Tube Heat Pump (Heating Mode)

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and

$$\mathrm{COP}_c = \frac{\tfrac{1}{2} f_A(\Delta H/M)_A \Phi_{B_d}}{\tfrac{1}{2} f_A(\Delta H/M)_A \Phi_{A_d} + \dfrac{Z + \rho_A C_A}{\rho_A} (1-\varepsilon_A)(T_H - T_{i_A}) + \dfrac{f_A(\Delta H/M)_A}{f_B(\Delta H/M)_B} \dfrac{Z + \rho_B C_B}{\rho_B} (1-\varepsilon_B)(T_{i_B} - T_L)} \qquad (2)$$

where

$$Z = \rho_t C_t (1 + f_v) \frac{d_o^2 - d_i^2}{d_i^2 - d_a^2} + f_v \rho_{enh} C_{enh} + r_f \frac{\rho_f C_f (1 + f_v) d_o^2}{(d_i^2 - d_a^2)}$$

and other symbols are defined in the list at the close of this paper. The regenerative effectiveness, ε_A and ε_B, is computed separately. Variation of the bundle and fluid temperatures, both spatially and with time, complicates the analysis of the regenerative heat-exchange process. A simplified computer model of this process, developed for the multi-tube heat pump, is described in Ref. 2.

We established a baseline design to be used in a parametric analysis of the COP; the parameters for this design are listed below. (Note that the design and the choice of hydrides have not been optimized in any sense. The resulting COP for the heating mode, computed using Eq. 1, is 1.12.)

Baseline-Design Parameters

Hydride A	$CaNi_5$	TL (P desorb)	40°F (1.06 atm)
Hydride B	$LaNi_5$	ε_A and ε_B	0.5
Heat-transfer fluid	Water	f_A and f_B	0.7
Tube material	Aluminum	d_o	0.75 in.
Enhancing material	Aluminum	Tube wall	0.083 in.
TH (P desorb)	205°F (5.67 atm)	r_f	0.5
T_{i_A} (P absorb)	105°F (0.91 atm)	f_v	0.5
T_{i_B} (P absorb)	105°F (5.51 atm)	d_a	(0.5)·(tube I.D.)

If the composite thermal mass (of the hydride, tube wall, enhancement, and fluid) of each bundle-end were zero, this would establish an upper limit on the COP. In this idealized case, Eqs. 1 and 2 reduce to expressions involving only the heats of absorption/desorption,

$$\mathrm{COP}_h = \frac{\Phi_{A_a} + \Phi_{B_a}}{\Phi_{A_d}} \qquad (3) \qquad \text{and} \qquad \mathrm{COP}_c = \frac{\Phi_{B_d}}{\Phi_{A_d}} \qquad (4)$$

The corresponding baseline-design COP for the heating mode is 1.80.

The Carnot heat pump provides another performance standard for comparison.(2) The Carnot COP, a function only of the unit design temperatures (T_H, T_{i_A}, T_{i_B}, and T_L), represents the maximum possible COP for any heat pump operating between these temperatures. For the heating and cooling modes, the Carnot COP is given by:

$$\mathrm{COP}_h = \frac{T_{i_A}}{T_H} + \frac{T_{i_B}}{T_H}\left(\frac{T_H - T_{i_A}}{T_{i_B} - T_L}\right) \qquad (5) \qquad \text{and} \qquad \mathrm{COP}_c = \frac{T_L}{T_H}\left(\frac{T_H - T_{i_A}}{T_{i_B} - T_L}\right) \qquad (6)$$

Using the baseline-design temperatures, we obtain a value of 2.16 for the heating-mode COP.

EXAMINATION OF HEAT-PUMP PARAMETERS

For the metal-hydride heat pump to become competitive, further development is required to improve performance and cut costs. The cost of the hydride material is by far the largest of the system's capital-cost elements.

For a given hydride pair, the maximum COP expected corresponds to the "zero-thermal-mass" case (Eqs. 3 and 4), so development must focus on approaching this ideal COP. Because analysis at ANL has dealt mainly with the heating mode of operation, we shall address only this mode.

Before selecting a hydride pair, one must define the design temperatures of the unit (T_H, T_{i_A}, T_{i_B}, and T_L). The temperature of the high-temperature heat source determines the value of T_H, while the intermediate temperatures, T_{i_A} and T_{i_B}, are related to the design value of the indoor temperature. The value of T_L depends on the design ambient (outdoor) temperature. For heat transfer, appropriate differentials must exist between these temperatures and their corresponding source/sink temperatures. The "zero-thermal-mass" COP_h cannot exceed the Carnot COP_h corresponding to the design temperatures.

With the design temperatures established, we next select suitable hydride pairs. The hydrides' properties must support an appropriate pressure differential between both beds, at the specified temperatures, to overcome flow resistances and permit hydrogen to flow freely in both directions over the cycle. Hydride pairs that meet this condition are further screened for such desirable properties as good kinetics, a wide pressure-plateau region (i.e., high $\Delta H/M$), minimal variation in pressure over the plateau, minimal hysteresis, and relatively low pressures at the design temperatures. (This last property influences tube structural design.) Other properties include low frangibility, to minimize particle carry-over to the opposite bed, and low relative cost.

Given design temperatures and a suitable hydride pair, the following quantities in Eq. 1 are fixed: Φ_{A_a}, Φ_{A_d}, Φ_{B_a}, $(\Delta H/M)_A$, ρ_A, C_A, ρ_B, C_B, T_H, T_{i_A}, T_{i_B}, and T_L. The remaining parameters are tube geometrical properties; densities and specific heats of tube material, enhancing materials, and fluid; regenerative effectiveness; and hydride-utilization fraction.

The hydride-utilization fraction, $f_{A,B}$ (the ratio of the actual mass of hydrogen absorbed/desorbed by a given mass of alloy to the maximum that could be absorbed/desorbed over the plateau region by that alloy mass), has a maximum value of one and represents a shortening of the plateau width ($\Delta H/M$). The fraction's value is governed by the fluid-to-bed heat-transfer characteristics, the kinetics of the hydriding reaction, and the time allotted to the absorption/desorption process. For the hydride pairs considered, heat-transfer rate rather than reaction rate has been the limiting factor. In the multitube heat pump, the time each bundle spends on the absorption/desorption segment of the cycle is set by the number of valve positions for these processes and the valve's rotational speed. Figure 4 shows the sensitivity of COP_h to the hydride-utilization fraction (assuming $f_A = f_B$). A change in $f_{A,B}$ from the baseline value of 0.7 to the maximum value (one) results in approximately a 10% increase in COP_h. (Here and in the following figures, Δ denotes the baseline-design value.)

Regenerative effectiveness $\varepsilon_{A,B}$, as noted, is determined using a separate computer model. We investigated the sensitivity of $\varepsilon_{A,B}$ to variations in film coefficient, number of bundles in the regenerative loop, valve time, and transit time. (Valve time is the period of time the valve spends in any bundle position. Transit time is the period of time required for a fluid particle to flow through a bundle and can be expressed in terms of flow velocity and flowpath length.) We found $\varepsilon_{A,B}$ to be relatively insensitive to the above parameters; it appears to maintain a value close to 0.5 in almost all cases. This value corresponds to the equilibrium temperature for simple mixing. Only when the transit time becomes large (>5 s) is any significant improvement noticed (see Fig. 5). However, limitations on minimum flow velocity and on bundle length (for residential applications) make transit times longer than 2 s difficult to achieve in any practical design. Figure 6 shows the sensitivity of COP_h to regenerative effectiveness (assuming $\varepsilon_A = \varepsilon_B$). Without regeneration (i.e., for $\varepsilon = o$) in the baseline design, the COP_h falls below 1.0, the minimum value for which a heat pump would be considered for heating applications. On the other hand, an increase in effectiveness from the baseline value of 0.5 to 0.7 (the apparent upper limit, approximately, for effectiveness) would mean a 12% increase in COP_h.

COP_h improves as regenerative effectiveness increases, but (by Eq. 1) the total heat output of the system per unit mass of hydride (represented by the numerator) decreases. The second term in the numerator of Eq. 1 equals the heat rejected to the indoors during completion of sensible cooling of the high-temperature bundle-ends.[2] Thus, a higher composite thermal mass (at the A-end) or a lower effectiveness (ε_A) results in increased output at the expense of a reduced COP_h.

Another important performance parameter is the fluid-volume fraction, r_f (the ratio of the fluid volume surrounding the tubes in a bundle-end to the volume of the tubes themselves). Because of its relatively high specific heat, the fluid contributes significantly to the composite thermal mass. Increased thermal mass degrades system performance, so bundle fluid volumes should be minimized by decreasing tube spacing within the bundle. (Note that reductions in tube spacing much beyond that corresponding to the baseline

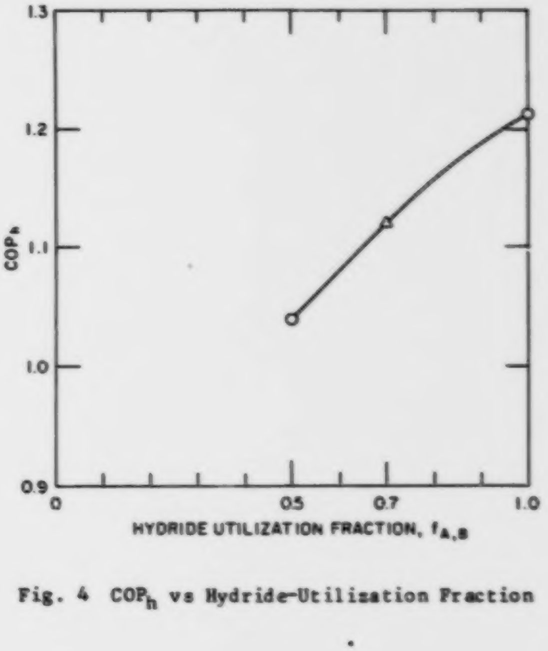

Fig. 4 COP_h vs Hydride-Utilization Fraction

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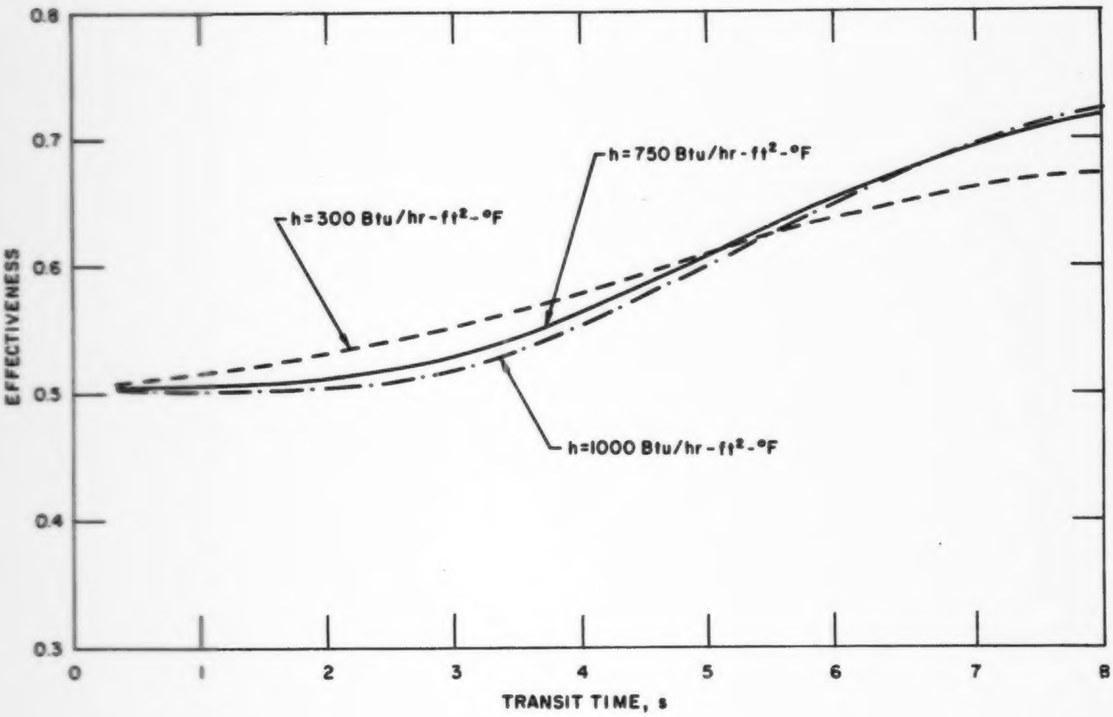

Fig. 5 Regenerative Effectiveness vs Transit Time

r_f value of 0.5 may worsen the bundle's thermal hydraulics.) The sensitivity of the COP_h to fluid-volume fraction is illustrated in Fig. 7. For the hypothetical case of $r_f = 0$, a dramatic improvement in COP_h is noted. Consequently, we are giving preliminary consideration to the idea of draining the fluid at each bundle-end prior to the sensible heating and cooling segment of the cycle. In this case, the hot or cold fluid would be replaced temporarily by fluid at some intermediate temperature. The mechanics of this scheme have yet to be worked out, but undoubtedly the design and control complexity of the multi-tube unit would be increased.

The low conductivity of hydride powder necessitates some form of enhancement to improve heat transfer between the fluid and the hydride bed. The enhancing material will comprise part of the composite thermal mass of a bundle-end. Because this material must be in intimate contact with the hydride powder, additional tube volume will also be required. One proposed method intersperses the hydride powder in a porous aluminum foam.

The influence of enhancement on thermal

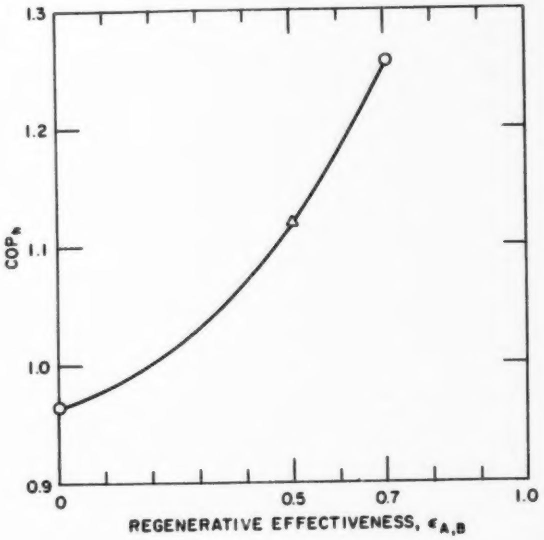

Fig. 6 COP_h vs Regenerative Effectiveness mass is reflected in the enhancement-volume fraction, f_v (the ratio of the enhancement volume to the volume of hydride powder in a tube). The sensitivity of COP_h to f_v is shown in Fig. 8. Very low values of f_v are hypothetical; the lower limit of f_v must be determined by an analysis of enhanced-bed heat-transfer characteristics.

To reduce thermal mass and improve fluid-to-bed heat transfer, tube-wall thickness must be minimized. The limiting wall thickness depends on the maximum internal (i.e., hydrogen) pressure during a cycle, the tube diameter, and the allowable tensile stress of the tube material. External-fluid pressure is approximately atmospheric. Figure 9 shows the sensitivity of COP_h to wall thickness for three standard 0.75-inch aluminum tubes. Decreasing the wall thickness from the baseline value of 83 mils to 28 mils yields a 10% increase in COP_h. The 28-mil thickness is more than sufficient to withstand the baseline maximum cycle pressure (approximately 6 atm).

What effect will the temperature of the high-temperature source have on COP_h? We answered this question by allowing T_H in Eq. 1 to vary while holding other parameters fixed. If the sign of the following quantity is positive, COP_h increases with increasing T_H; if negative, COP_h decreases:

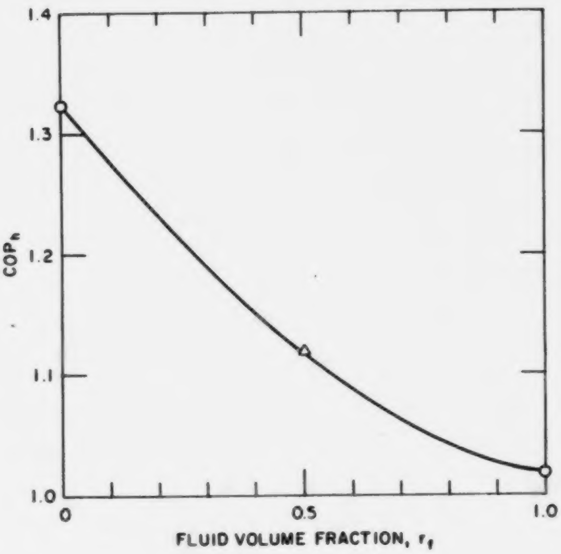

Fig. 7 COP_h vs Fluid-Volume Fraction

$$\left[(\Phi_{A_d} - \Phi_{A_a}) - \Phi_{B_a} + 2\left(\frac{Z + \rho_B C_B}{\rho_B}\right)\frac{(1-\varepsilon_B)(T_{i_B} - T_L)}{f_B(\Delta H/M)_B}\right] \begin{cases} > 0 \Rightarrow COP_h \text{ increases,} \\ < 0 \Rightarrow COP_h \text{ decreases} \end{cases} \tag{7}$$

For the baseline-design parameters, this quantity is negative, so there would be a disadvantage in seeking a higher-temperature source. A similar analysis of the sensitivity of COP_h to variations in the

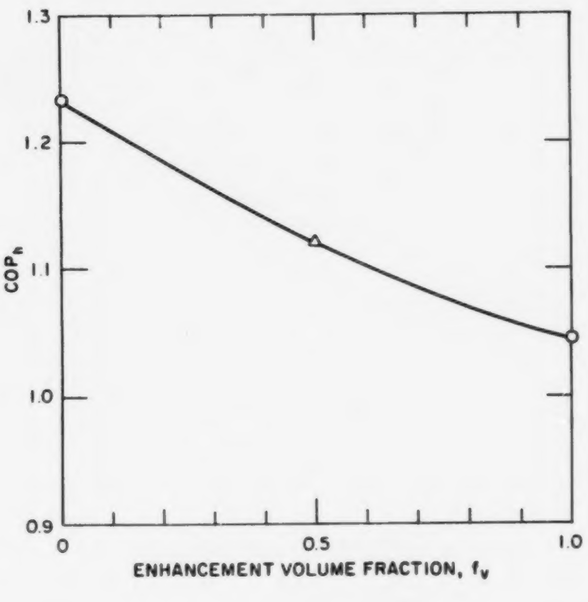

Fig. 8 COP_h vs Enhancement-Volume Fraction

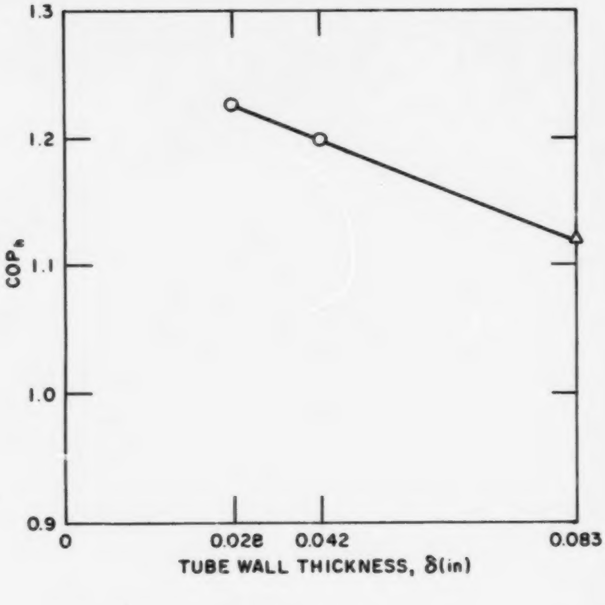

Fig. 9 COP_h vs Tube-Wall Thickness

minimum cycle temperature, T_L, indicated that as T_L is increased, the COP always increases. However, because T_L must be less than the design-value outdoor temperature, increasing T_L would narrow the heat pump's operating-temperature range.

We also examined the sensitivity of the COP to variations in plateau width ($\Delta H/M$) for both the high- and low-temperature hydrides, finding that as $(\Delta H/M)_B$ is increased, the COP always grows larger, whereas an increase in $(\Delta H/M)_A$ could either increase or decrease COP. The latter (A) case's behavior is governed by the reverse of the inequalities given in Eq. 7. For the baseline design, an increase in $(\Delta H/M)_A$ resulted in an improved COP. To minimize hydride material requirements, and thus capital cost and unit size, plateau widths for both hydrides should be as large as possible, as should the hydride-utilization fraction.

Our results, over-all, delineate performance trends as system parameters are varied (individually) from their specified baseline values. These analyses, although useful in identifying areas where design improvements can be made, are only a first step. Subsequent efforts will require computerized optimization of the system.

To see the potential for improving COP_h, consider the following changes in parameters relative to their baseline values: By improved fluid-to-bed heat transfer, $f_{A,B}$ is increased to one; tube-wall thickness is 28 mils; f_v is reduced to 0.10; r_f (perhaps by draining the fluid before sensible heating and cooling) is reduced to, say, 0.20. By making these changes, one increases COP_h from a baseline value of 1.12 to 1.52. (The limiting value for the baseline-design hydride pair, corresponding to the "zero-thermal-mass" case, is 1.80.)

FUTURE ACTIVITIES

Future analytical efforts at ANL will involve continued development, refinement, and programming of system-performance algorithms for the multi-tube unit. We will emphasize the system's thermal hydraulics--specifically, predictions of coolant-to-bed heat transfer, thermal gradients, and hydrogen and coolant pressure drops. Also, ANL will begin system-optimization work and development of cost algorithms.

DEFINITION OF SYMBOLS

A and B are subscripts for high- and low-temperature hydrides.

HYDRIDE PROPERTIES

$\Phi_{A,B_{a,d}}$	Heat of absorption or desorption
$(\Delta H/M)_{A,B}$	Pressure-plateau width
$\rho_{A,B}$	Hydride density
$C_{A,B}$	Hydride specific heat

OPERATING TEMPERATURES

T_H	High temperature
T_{i_A}, T_{i_B}	Intermediate temperatures
T_L	Low temperature

GEOMETRIC PARAMETERS

d_o	Tube outer diameter
d_i	Tube inner diameter
d_a	Hydride-annulus inner diameter
r_f	Fluid-volume fraction (of tube vol.)
f_v	Enhancement-volume fraction (of hydride vol.)

TUBE- AND ENHANCING-MATERIAL PROPERTIES

ρ_t	Tube-material density
ρ_{enh}	Enhancing-material density
C_t	Tube-material specific heat
C_{enh}	Enhancing-material specific heat

FLUID PROPERTIES

ρ_f	Fluid density
C_f	Fluid specific heat

OTHER

$\epsilon_{A,B}$	Regenerative heat-exchange effectiveness
$f_{A,B}$	Hydride-utilization fraction

REFERENCES

1. J.M. Clinch, H.I. Abelson, J.S. Horowitz. Design and Performance of a Multi-Tube Metal-Hydride Heat Pump. Thermal and Chemical Storage Annual Contractors' Review Meeting, McLean, Va., October 13-17, 1980.

2. H.I. Abelson and J.S. Horowitz. Thermodynamic Analysis of a Metal-Hydride Heat Pump. Journal of Energy, July/August 1981.

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TES FOR BUILDING HEATING & COOLING

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PROJECT SUMMARY

Project Title: The ORNL Thermal Energy Storage Program

Principal Investigator: James F. Martin

Organization:
Oak Ridge National Laboratory
P.O. Box Y
Bldg. 9204-1, MS-3
Oak Ridge, Tennessee 37830

Project Goals: The overall goal of the program is the development of advanced thermal energy storage technologies directed towards residential and commercial building heating and cooling and industrial applications. Research and development is conducted to develop effective, low cost thermal storage materials and subsystems for defined application areas. Systems utilizing both latent and sensible heat storage will be developed. Thermal energy sources include industrial process reject heat, utility waste heat, solar energy, and electricity available off-peak or at reduced demand. Specific application areas include utility load management, passive and active solar, on site and off site industrial applications, and premium fuel displacement.

Project Status: Results of a study of TES practices and benefits in the U.S. and Scandinavian pulp and paper industry were incorporated into a seminar series for the industry. A study of inexpensive substitutes such as rock, taconite, etc. for ceramic storage bricks in electrically charged storage furnaces was concluded with no economic advantage of storage devices utilizing alternative materials over conventional storage furnaces shown. Preliminary results from a study of technical and economic performance of phase change materials storage with heat pumps, have identified the most promising configurations and materials for further development. Off-peak/on-peak electrical rate structures where heat pump storage is competitive with the heat pump alone have been delineated. Phase II of the Bellingham District Heating Program is complete and results show that utilization of industrial reject heat for district heating is technically and economically viable. New programs were initiated in the field of cool storage for residential applications, latent heat storage for passive solar applications and advanced storage for reuse of process heat in the brick, tile, and ceramic industry.

Contract Number: 00001 (16)

Contract Period: Oct. 1980 - September 1981

Funding Level: $4,700,000

Funding Source: Department of Energy, Division of Energy Storage

ORNL THERMAL ENERGY STORAGE PROGRAM OVERVIEW*

J. F. Martin
Engineering Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

Development of Thermal Energy Storage technologies and subsystems is relevant to national energy objectives in both energy conservation and the deployment of new energy sources. Oak Ridge National Laboratory, acting for DOE as a Lead Technical Laboratory in the areas of building heating and cooling and industrial applications, supports the national objectives through the program described. Specific subcontract and in-house activities are summarized, and the results of research conducted during FY 1981 are given. The major thrust of next year's program is given.

INTRODUCTION

The Oak Ridge National Laboratory (ORNL) acts for the DOE Office of Energy Systems Research, Division of Energy Storage (STOR), as the Lead Technical Laboratory for research and development in prescribed areas of Thermal Energy Storage (TES). The ORNL/TES program is focused on the dual thrusts of building heating and cooling applications and industrial applications. These activities relate to the DOE/STOR total program as shown in Figure 1. The objective of the program is to conduct the research and development which is required to establish a base technology for reliable, low cost, high performance TES devices. Such devices make feasible the use of thermal energy sources whose times of availability are significantly disparate with their times of use, thereby greatly increasing the opportunities for national energy conservation. The objective of the program is pursued in specific application areas. The general application targets are identified in Figure 2 in each of the two main thrusts of the ORNL/TES program.

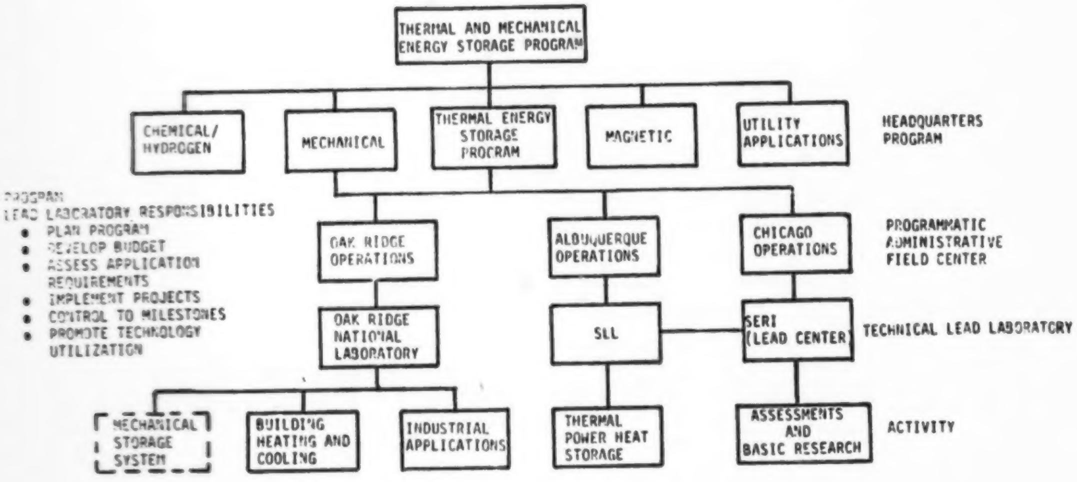
THERMAL AND MECHANICAL ENERGY STORAGE PROGRAM
CHEMICAL/ HYDROGEN
MECHANICAL
THERMAL ENERGY STORAGE PROGRAM
MAGNETIC
UTILITY APPLICATIONS
HEADQUARTERS PROGRAM
PROGRAM LEAD LABORATORY RESPONSIBILITIES
• PLAN PROGRAM
• DEVELOP BUDGET
• ASSESS APPLICATION REQUIREMENTS
• IMPLEMENT PROJECTS
• CONTROL TO MILESTONES
• PROMOTE TECHNOLOGY UTILIZATION
OAK RIDGE OPERATIONS
ALBUQUERQUE OPERATIONS
CHICAGO OPERATIONS
PROGRAMMATIC ADMINISTRATIVE FIELD CENTER
OAK RIDGE NATIONAL LABORATORY
SLL
SERI (LEAD CENTER)
TECHNICAL LEAD LABORATORY
MECHANICAL STORAGE SYSTEM
BUILDING HEATING AND COOLING
INDUSTRIAL APPLICATIONS
THERMAL POWER HEAT STORAGE
ASSESSMENTS AND BASIC RESEARCH
ACTIVITY

Fig. 1. ORNL Energy Storage Program Organization and Responsibilities

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*Research sponsored by the Division of Physical and Chemical Energy Storage Systems, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation-Nuclear Division.

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	PROGRAM THRUST	
	BUILDING HEATING AND COOLING APPLICATIONS	INDUSTRIAL APPLICATIONS
APPLICATION TARGETS	• PASSIVE SOLAR SYSTEMS • PCM's IN BUILDING MATERIALS • AUGUMENTED THERMAL TRANSPORT WALLS • ACTIVE SOLAR SYSTEMS • ADVANCED PCM MATERIALS • ADVANCED SENSIBLE HEAT • UTILITY LOAD MANAGEMENT SYSTEM FOR RESIDENTIAL APPLICATIONS • ELECTRIC STORAGE FURNACE • HEAT PUMP TES (HOT) SYSTEMS • HEAT PUMP TES (COOL) SYSTEMS • COOL STORAGE (ICE) SYSTEMS • EARTH STORAGE • UTILITY LOAD MANAGEMENT SYSTEMS FOR COMMERCIAL APPLICATIONS - SENSIBLE HEAT	• ONSITE REJECT HEAT UTILIZATION • DIRECT CONTACT HIGH TEMPERATURE SYSTEMS • MODERATE TEMPERATURE SYSTEMS • SENSIBLE HEAT STORAGE SYSTEMS • OFFSITE REJECT HEAT UTILIZATION (DISTRICT HEATING APPLICATIONS) • INDUSTRIAL SOLAR PROCESS HEAT • HIGH TEMPERATURE SYSTEMS • MODERATE TEMPERATURE SYSTEMS • LOW TEMPERATURE SYSTEMS • PREMIUM FUEL DISPLACEMENT SYSTEMS
PROGRAM CONTENT	SYSTEM ANALYSIS AND EVALUATION TES MEDIA RESEARCH AND DEVELOPMENT TES SUBSYSTEM RESEARCH AND DEVELOPMENT TECHNOLOGY TRANSFER	

Fig. 2. ORNL TES Program Research and Development Program Activities

BUILDING HEATING AND COOLING

Included under building heating and cooling are four application target areas. Two of these are concerned with TES development for utility load management: systems applicable to residential building use, and those applicable to commercial building use. The specific objective for these two application targets is the reduction of oil and gas consumption through shifting electric utility load from peaking to base load generating equipment. The widespread use of customer-side-of-the-meter TES is a means of achieving this goal. Development of technologies for such devices is a major part of the ORNL/TES program.

Research Triangle Institute (RTI) is conducting a program of economic and technical analysis to evaluate a wide range of heat pump coupled latent heat storage systems for residential space heating and cooling. This study, the second phase of an on-going program, was initiated this year and will be concluded in mid FY 1982. A preliminary screening of twenty-two configurations has been completed, followed by selection of fourteen systems for analysis by a modified version of conventional heat pump bin analysis techniques. The analysis was carried out for each system at three climatic conditions. Both a load-shifting control which maximizes shifting energy use from on- to off-peak and a load leveling control which reduces energy demand were simulated. Results have been generated which define the region of off-peak/on-peak rates when each system has an advantage in life cycle costs over a standard heat pump. Annual (steady state) Coefficients of Performance (COP) of storage heat pumps are shown to be competitive with those of the heat pump without storage.

A program has been initiated with Carrier Corporation for the first phase of a development effort leading to design of a prototype residential ice storage system. Laboratory research will address problems such as ice inventory control, climate sensing, coil design, and container configuration. Technical problems encountered in recent field tests of prototype units have confirmed the need for this research effort. The program also seeks, through a utility industry-wide survey, to determine future utility off-peak rate trends as well as their needs for load control in summer peaking situations. Surveys of public opinion to provide information on unit size and installation constraints and to determine the value of storage for setting cost goals are also included in the program.

Several programs are addressing the technology of energy stored as sensible heat in solids. As part of the technology transfer activity of the ORNL/TES program, a test facility has been operated at the Herrick Laboratories of Purdue University for two years. Testing of electrical resistance element charged heat storage devices is conducted for the purpose of developing test procedures and test components and for establishing the thermal performance of prototype thermal storage furnaces. Contributions to the applicable ASHRAE test procedure have been made over the past year, and liason with ASHRAE is maintained in order that developments in testing methodology may be made available to the Society. Comparisons of thermal performance of imported olivine and magnesite storage bricks and domestically produced prototype olivine bricks have been made. Results of these comparisons indicate that the performance of magnesite and olivine bricks is quite sensitive to processing parameters so that the benefit of the elevated thermal properties of magnesite may not be realized if the quality of the magnesite brick industry production is not maintained at a high level.

North Carolina State University has developed storage bricks of North Carolina olivine under internal sponsorship. The ORNL/TES program is supporting an experimental program of evaluation of the thermal and mechanical performance of these prototype bricks. Tests are being conducted to determine brick internal temperature distribution under dynamic conditions, temperature distributions in storage furnace assemblies of brick under charge/discharge conditions, and the effects of thermal cycling on mechanical properties.

The University of Washington is funded to investigate chemically-bonded Washington State olivine as a material for sensible heat storage. Previous studies at the University have identified cementitious binders which show considerable promise for this application. The program is seeking to identify the most promising formulations of olivine and binder and to determine the feasibility of utilizing these materials as thermal storage components. A successful development has the promise of providing a lower cost brick over those presently available, because the chemical bonding fabrication process circumvents the energy intensive firing process of ceramic brick manufacture.

A complementary program is to be funded with Materials Consultant Associates, Inc. for development of bonded fabrication techniques which utilize North Carolina olivine. Binding materials, compaction techniques and curing cycles, different from those used in the University of Washington research, will provide additional chance for successful development of a suitable storage material.

TRW has completed a study of solid storage materials which are alternatives to storage bricks. They have identified economically attractive materials, determined the thermal and physical properties of such materials, and simulated their performance as heat storage materials in a packed bed/air discharge system. Several technical problems would have to be solved before a packed bed system would be feasible. No cost advantage over the ceramic brick storage furnace was shown.

Several programs are sponsored which involve the collection and analysis of data showing the performance of stratified water storage. As a part of the technology transfer function of the ORNL/TES program, results of carefully conducted, highly instrumented tests of operating systems will be made available to the designers and users of storage systems.

The University of New Mexico is funded in a program, which also received support form EPRI, to measure the performance of a labyrinth storage tank in maintaining thermal stratification. The operating system is in the University of New Mexico Mechanical Engineerinng Building. Both hot storage from a solar collector system and hot and cold storage from off-peak heat pump charging are incorporated in the system. The system is operating and data are being recorded. Preliminary results show that the integrity of the thermocline maintained by the labyrinth is less than expected, and tank modifications are anticipated.

A similar program is being conducted by the University of Tennessee. Cool water storage in a public school building is supplied from off-peak operation of a chiller, while hot water storage is supplied from either an electric boiler or from chiller reject heat. Stratification is maintained by a water tight membrane. The data collection phase will start this fall.

A third program to collect data from a naturally stratified water tank storage system will be initiated in early FY 1982. This program, which will be conducted by RTI, is a cooperative effort between the North Carolina Alternative Energy Corporation and ORNL.

Natural temperature stratification is being studied at Argonne National Laboratory under an ORNL/TES contract. The influence of inlet and outlet diffuser configurations on the thermocline gradient is being investigated. A semi-empirical model of stratification has been development, and experimental measurements to validate the model are being conducted.

A survey of operational commercial, non-solar, hot and cool storage systems in the U.S. and Canada by Franklin Research Center has uncovered technical information on approximately 300 installations. The data from the survey will be published by ASHRAE to give it general distribution. A follow-on effort will be the selection of six installations from which detailed cost and performance data can be obtained to provide a more detailed performance measure for storage system designers.

Two application target areas address passive and active solar applications of TES. The specific objective of projects in these areas is to develop storage technologies which promote oil and gas conservation through the use of TES to increase the fraction of building heating and cooling loads which can be met with solar energy.

Two programs were sponsored during this year. Pennwalt Corporation is developing techniques for encapsulation of heat of fusion storage materials in small [0.3 - 1.3 cm (1/8 - 1/2 inch)] diameter pellets for use in packed bed storage devices as well as for incorporation in building materials. Materials which are effective for storage temperatures of 23°C to 49°C (73°F to 120°F) have been successfully encapsulated in coatings of various latex formulations. Laboratory-scale beds of pellets have been subjected to over 1700 thermal cycles successfully. Costs of large scale production of the material have been projected to be 40¢ per pound. Further, large scale cycling tests to obtain long term stability, heat storage capacity, and heat transfer efficiency is planned.

Under contract to Argonne National Laboratory, Calmac Corporation has previously developed three TES units: a 7°C (45°F) storage unit for residential cool storage, a 46°C (115°F) storage unit for solar heat storage, and a 115°C (240°F) storage unit for absorption air conditioning storage. Problems of incongruent melting of the PCM used in the 115°C (240°F) unit (sodium thiosulfate) and the 46°C (115°F) unit (Glauber salt eutectic) have not been satisfactorily solved. The ORNL/TES program is sponsoring additional research by Calmac to determine the effectiveness of additives to prevention of stratification of the PCMs. Effects on stratification, rate of crystal growth, subcooling, fusion temperature, and latent heat capacity are to be determined.

An additional program in passive solar heating storage is being developed through an RFP soliciting concepts for the inclusion of PCM into building materials. Research and development resulting from proposals received in response to this solicitation will be initiated in early FY 1982.

INDUSTRIAL APPLICATIONS

The second major thrust of the ORNL/TES Program is the development of TES technology for industrial applications. Four application target areas are identified for this part of the program. Two target areas are aimed at utilization of industrial process reject heat: storage for utilization external to the plant boundary, and storage for utilization within the plant boundary. The specific goals for these target areas is the conservation of energy through recovery, storage, and reuse of process reject heat.

The technology of storage of reject heat for external use is addressed in two district heating projects.

Phase II of the Bellingham District Heating Project was completed by Rocket Research Company in mid-FY 1981. The goal of this phase was to establish the feasibility of a district heating system in the City of Bellingham, WA. Reject heat from the Intalco Aluminum plant adjacent to the city will furnish hot water to the system. The project addressed five tasks: a market analysis, a technology review, identification of alternative energy sources, institutional considerations, and system performance.

The results of Phase II were favorable. The City of Bellingham, Rocket Research Company, and Trans Energy, Inc. are formulating plans for an 8-block demonstration heating system which will function as a test of full system cost and performance. The ORNL/TES program is sponsoring a small effort by Trans Energy, Inc. in support of this planning to define the impact of various storage/distribution configurations on the operation of the district heating system.

Rocket Research Company is funded for a Phase III effort consisting of sub-scale heat exchanger tests in the Intalco plant fume duct. This effort addresses the heat exchanger fouling and corrosion problems identified in Phase II as well as the definition of the effect of withdrawing heat from the fume duct stream on the plant pollution control equipment. This project will continue in FY 1982 at a level which is consistent with the ORNL/TES program funding.

An RFP will be issued late this fiscal year for technical support for the HUD/DOE national district heating plan. The contractor selected will evaluate the role of TES in site-specific district heating systems selected from the cities participating in the HUD/DOE program. A conceptual TES design and cost/benefit analysis of each site chosen for analysis will be made available to the HUD site evaluation team for use in assessment of the feasibility of district heating and cooling.

A program has been initiated with the Institute of Gas Technology to develop an advanced TES media for high-temperature reject heat recovery. Efforts are focused on a composite medium composed of a phase-change carbonate salt supported within the capillary structure of a particulate ceramic matrix of porous sintered ceramic. Thermal and mechanical performance requirements will be drawn from an analysis of reject heat sources and use opportunities in the brick, clay, and ceramic industry. Phase I of the program will address material selection and developmental testing of the media, a benefit analysis for the chosen industry, component and subsystem development, and a site-specific prototype testing plan. This is a multi-year program.

An RFP will be issued early next year for research and development of advanced thermal storage technology directed toward industrial applications. Phase I will consist of identification of a storage concept and its industrial application, a system definition, an economic analysis to show required goals and benefits and storage unit developmental testing. Successful development of a storage unit in Phase I will be followed by a storage system development.

A program of technology transfer of TES practice in the pulp and paper industry is being conducted by H. Edde, Inc. The target of this element of the industrial applications program is premium fuel displacement by use of process reject heat. Foreign and domestic mills employing TES for conservation were identified, and five were selected for detailed analysis of investment and operating costs of the TES system. Cost benefit analyses were made and energy savings were estimated. The generalized results of these analyses are being presented in two seminars to the U.S. pulp and paper industry this Fall.

TECHNICAL SUPPORT

In-house technical support to the program is in the areas of mathematical modeling of thermal storage systems, analysis of heat transport phenomena, operation of testing facilities, experiments in the extraction and use of earth-stored-heat in conjunction with heat pumps, and assessments of research and development needs.

Over a large part of the U.S., the temperature of the earth a few feet below the surface is sufficiently above average winter ambient that a benefit could accrue from its utilization for pre-heating heat pump inlet air. That this heat can be made available from the crawl space of a house has been shown in experiments conducted by ORNL. Preparations for an experiment which will quantify the effects of this pre-heating on heat pump cycling, defrost cycle, and capacity and on the use of auxiliary resistance heating, are complete. Experiments to establish benefits in performance will extend over the next two years.

The ORNL thermal cycle test loop has been used to subject the ASHRAE test standard 94-77 to a practical test of effectiveness. A program utilizing this facility is being conducted in cooperation with Argonne National Laboratory to establish specific testing procedures for solar thermal storage devices.

PROJECT SUMMARY

Project Title: TES/Heat Pump Performance Evaluation

Principal Investigator: Tony W. Sigmon
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Organization: Research Triangle Institute
Energy Systems Department
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Project Goals: Identify global functional requirements of cost-effective heat pump coupled latent heat thermal energy storage (TES) systems for residential space heating and cooling applications. Complete detailed analyses to project changes in performance and cost that may result from changes in system design parameters.

Project Status: Four primary tasks have been identified for completion. These include:

(a) development of a natural convection heat transfer model for the phase change material
(b) completion of a TES/heat pump bin analysis
(c) modify existing steady state TES/heat pump simulation and execute to identify changes in performance that occur with changes in design parameters
(d) modify existing hourly operational performance simulation and execute to determine changes in operational performance that occur with changes in application scenario

Problem formulation has been completed for Task (a). The software has been developed and is currently undergoing a debugging process. Limiting case of constant wall temperature has been completed and satisfactorily compared to experimental data provided by ORNL.

Task (b) has been completed and used to project the energy consumption of various system configurations at selected climatic conditions. These results have then been used to compute system life cycle cost and to select optimum systems based on a minimum life cycle cost scenario. The simulation package is currently being modified to reflect those changes suggested by these initial results.

The final two tasks await completion of Tasks (a) and (b).

Contract Number: 62B-13835C

Contract Period: December 1980 through December 1981

Funding Level: $192,000

Funding Source: U.S. Department of Energy through Oak Ridge National Laboratory

TES/HEAT PUMP PERFORMANCE EVALUATION

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ABSTRACT

A technique has been developed that utilizes a modified version of the conventional heat pump bin procedure to project energy use by TES/heat pump and conventional heat pump systems. The intent of the effort is to provide information that can be used to evaluate various program alternatives in regard to the development of TES/heat pump systems. The modified bin procedure has been used in conjunction with an annualized life cycle cost algorithm to evaluate each system from both a technical and economic perspective. As a final step three levels of analysis have been completed to identify the system or systems with the lowest LCC for various application scenarios. These efforts will be extended by completing more detailed analyses of the steady state performance and operation of selected systems.

INTRODUCTION

The following is a description of the approach followed along with the results and conclusions obtained from a technical and economic analysis of heat pump coupled thermal energy storage (TES) systems for residential space heating and cooling applications. The primary objective of the study has been to identify the system level functional requirements of latent heat TES/heat pump systems. These functional requirements have been defined for three climatic regions and two control scenarios in terms of storage type (heating, cooling or dual), system configuration, heat pump size and storage material melt temperature. Thirteen different TES/heat pump configurations have been considered which define not only the type of storage available but also the conceptual system design, which is dictated by various charge/discharge options. The configuration types have been categorized by the method used to charge and discharge the TES subsystem. These classifications are as follows:

Direct - Heat transfer between an air stream and the TES material

Indirect - Heat transfer between a refrigerant and the TES material

Intermediate - Heat transfer between an intermediate fluid (water) and the TES material.

A summary of the various configurations considered is given in Table 1. Combining these variations in configuration with the number of heat pump sizes and storage materials considered results in eighty-four (84) possible system combinations including baseline conventional heat pump systems. A total of 360 combinations of system, site and control strategy were considered.

MODIFIED BIN ANALYSIS

Annual energy use has been projected using a modified version of the bin procedure used to estimate energy use for conventional heat pump systems. The modified form of this procedure provides for differences in seasonal as well as on- and off-peak operation of the systems including charging and discharging of the storage system. This technique accepts as input the annual ambient temperature distribution in 5°F increments (bins), building thermal load characteristics and system steady state performance data as a function of these bins, and information describing a time-of-day electric rate structure. This informaton is then merged through a control algorithm to determine energy use by mode of operation, rating period and season.

Two system control strategies have been defined for the TES/heat pump systems. Load shifting control is used to maximize the shift in energy use and demand from the on-peak to off-peak hours while under a load leveling control strategy the system seeks a uniform energy use pattern over the entire day by shifting only a portion of the on-peak load to the off-peak period. Conventional heat pumps have been assumed to operate on demand under a conventional electrical utility rate structure.

Three locations across the United States have been considered in the analysis: Boston, MA; Miami, FL; and Nashville, TN. Hourly meterological data for a "typical" meterological year at each site have been used to determine the frequency of occurrence of each ambient temperature bin on a seasonal as well as on- and off-peak basis. This meterological data has been provided by Sandia National Laboratory through the SOLMET meterological data files.

Configuration No.	Heating Mode Charging/Discharging	Cooling Mode Charging/Discharging	Storage Material	Melt Temperature (°F)
1	Indirect/Direct	None	SIP	114
2	None	Indirect/Direct	Ice Calmac	32 45
3	Indirect/Indirect	None	Calmac Delaware Glauber Salt Thermol 81	45 55 81
4	None	Indirect/Indirect	Calmac Delaware Glauber Salt Thermol 81	45 55 81
5	Indirect/Intermediate	None	SIP	114
6	None	Indirect/Intermediate	Ice Calmac	32 45
7	Direct/Direct	None	Delaware Glauber Salt	90
8	None	Direct/Direct	Calmac	45
9	Indirect/Indirect	Indirect/Direct	Calmac	45
10	Indirect/Indirect	Indirect/Indirect	Calmac Delaware Glauber Salt	45 55
11	Sensible Indirect/ Intermediate	Indirect/Direct	Ice Calmac	32 45
12	Sensible Indirect/ Intermediate	Indirect/Intermediate	Ice Calmac	32 45
13	Sensible Indirect/ Intermediate	Direct/Direct	Calmac	45

Table 1. TES/Heat Pump Configurations

Average thermal loads at each bin have been determined for each site based on hourly sensible and latent heat building thermal loads which had been previously computed for a typical residential structure at each site. TRNSYS, a transient simulation program prepared by the Solar Energy Laboratory at the University of Wisconsin-Madison was utilized in determining these loads.

Steady state performance characteristics, i.e., capacity and input power required to drive the system during each possible mode of operation, have been computed for each of the TES/heat pump and conventional heat pump systems. The number of systems and performance parameters considered necessitated that a simplified approach be followed in developing performance characteristics. Earlier efforts by RTI have focused upon the development of steady state performance characteristics for a small set of configuration types, and to the extent possible, these prior results have been utilized to project the performance characteristics of other designs considered in the analysis. A more detailed analysis has been completed for those configurations to which prior results could not be extended.

Characteristic TOD rate structures have been identified for each location based on presently available rate structures in the geographic area surrounding each site. Daily divisions of on- and off-peak periods are identical for each site; however, the division between winter and summer months are site dependent. Operating costs of the TES systems have been determined using the energy use characteristics resulting from the bin analysis for a reasonable range of values for on- and off-peak energy charges. Operating costs for the conventional heat pump systems have been computed for a range of conventional electricity rates.

Operational performance of the baseline 3-ton heat pump and four of the TES/heat pump systems presented in Table 1 has been projected utilizing the modified bin procedure and compared with results of hourly simulations previously conducted.[1] This comparative analysis provdes a means of assessing

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the extent to which the assumptions and inadequacies of the bin procedure affect system energy use characteristics. The intent has been to determine if the ranking of the systems in terms of ability to shift energy and total energy consumption remains the same. Therefore, the two methods have been compared based solely on the operational performance of the systems. The results of these two analyses are in fact comparable in regard to these energy use characteristics, with differences of less than 5% noted in most cases. Larger differences are attributable to differences in the manner in which storage capacity was treated in each case. For the hourly simulation, design storage capacity was a constant input value while the bin procedure determines a design storage capacity based on the largest net charge or discharge required during the course of the peak day.

SYSTEM ECONOMICS

Installed costs for each system have been determined based on current component costs. Prior studies[2] have been utilized to the extent possible in arriving at these costs while conventional cost engineering methodologies were used in those cases when additional information was required. For the TES/heat pump systems considered these costs did not assume mass manufacturing techniques were available, but that in each case only a small number of systems were to be built. For this reason heat pump and TES/heat pump costs are not consistent and should be compared only after proper consideration of this factor.

The cost of ownership has been determined for each system, site, and control scenario considered based on the life cycle cost (LCC) associated with the purchase and operation of the system. The LCC analysis considers total costs over the life of a system by applying a capital recovery factor to present value costs to convert them to an equivalent stream of annual costs. The energy use characteristics projected with the bin technique have been combined with computed capital cost for each system to determine the annualized life cycle cost associated with the purchase and operation of the various alternatives.

RESULTS AND CONCLUSIONS

The results of the bin procedure and the life cycle cost analysis have been analyzed from the perspective of cost of ownership and through consideration of projected energy demand and use characteristics. The systems were evaluated from an operational point of view in terms of seasonal performance factors (SPF), total on-peak energy use and system load factor. Three levels of economic analysis have been completed to identify the system or systems with the lowest life cycle cost within a single configuration, within each storage category (heat, cool, dual) and finally the overall lowest cost system from among the many alternatives available. This analysis has been carried out for each climatic region and control scenario considered.

Figure 1 shows the final results of this analysis for the Nashville climatic area for the load shifting control algorithm. Two types of output are presented in each figure. The first is a plot showing the regions of the R_{on} (on-peak energy charge) and R_{off} (off-peak energy charge) array where particular systems have the lowest LCC of all systems considered. These regions are distinguished by the heavy solid lines. The value of LCC for these optimal systems, which are also a function of R_{on} and R_{off}, are depicted on the same plot by dashed lines showing LCC contours (lines of constant LCC). The following format will be used in denoting a specific system:

Configuration No./Heat Pump Size/Melt Temperature

For example, 1/4/114 would denote a system corresponding to Configuration 1 with a 4-ton heat pump and a melt temperature of 114°F. Directly below the system designation is the value for the peak day storage capacity.

For load shifting control in Nashville both heating and cooling storage systems appear on the optimum life cycle cost plot. To a certain extent this is a reflection of the balanced heating and cooling loads at this site. System 2/4/32 has a relatively high seasonal performance factor, low on-peak energy use and low storage material costs and is therefore the most cost-effective cooling storage system. System 7/4/90 is the least capital intensive heating storage system that meets the 4-ton design cooling load and for primarily this reason is the most cost effective of the heating storage alternatives. System 2/4/32 with its high SPF is the most cost effective system at high energy charges while at low energy charges 7/4/90 with its low capital cost has the lowest LCC.

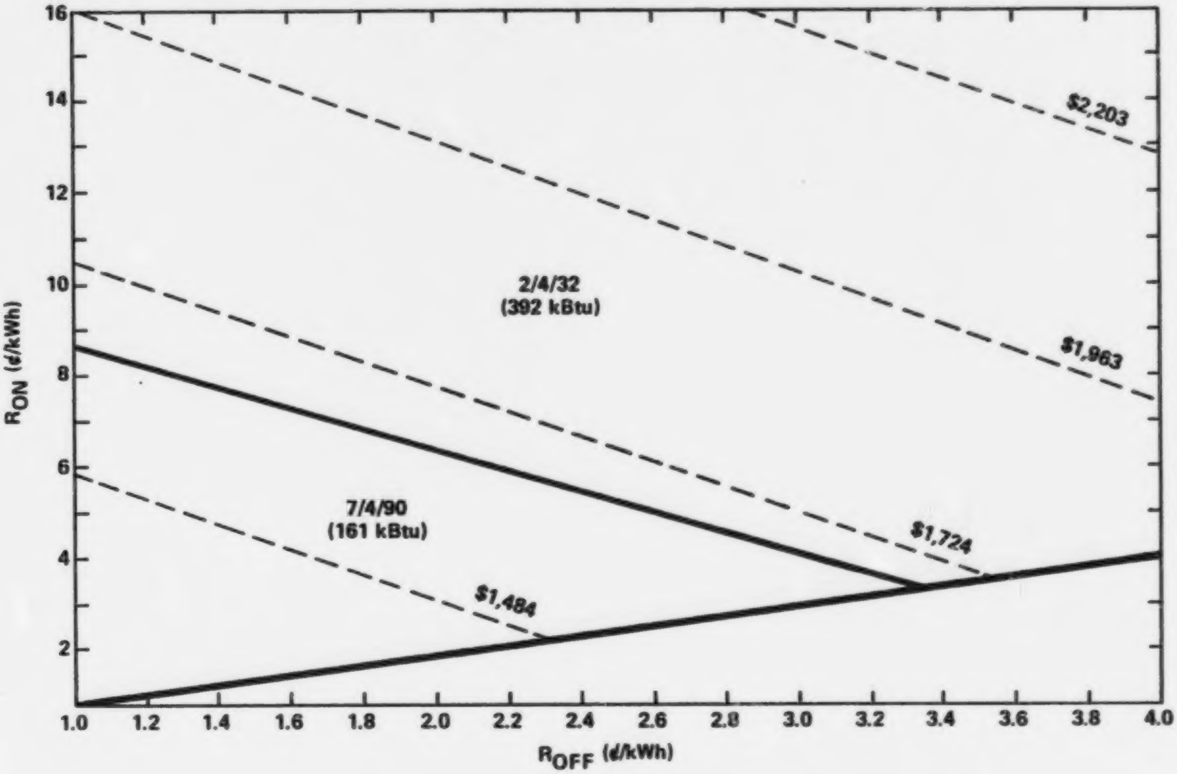

Figure 1. Optimum Load Shifting Systems (Nashville)

Load shifting systems are least constrained in shifting energy use at high on-peak, low off-peak load conditions and are most effective when the corresponding off-peak ambient conditions are most conducive to efficient charging operation, i.e., low ambient conditions for cooling systems. At sufficiently low thermal load or system discharging conditions, no extra benefit is received by increasing heat pump size in an attempt to shift energy use by using storage. An increase in heat pump capacity beyond this point may, however, result in a displacement of resistance heating requirements. On the other hand, at high load conditions it becomes important to increase discharging capacity and heat pump size, ideally to the point where the entire on-peak load is shifted.

The relative cost effectiveness of different load shifting systems is determined by tradeoffs between capital costs and energy use characteristics. At low energy costs LCC is more sensitive to capital cost than total energy use. At high energy costs, however, the overall energy efficiency of the system is the more significant factor. For high heating load climates, it is most cost effective to increase heat pump size in order to displace resistance heating. In these cases storage cooling is a second order issue. In the other extreme, at low heating environments, the usefulness of heating storage is minimized.

An advantage of the load leveling control scenario is that for cooling storage systems there is a trade-off between heat pump size and storage capacity. Since discharging occurs coincidentally with heat pump cooling, the effective system cooling is greater than that for the same size heat pump operating independently. Therefore storage capacity can displace heat pump capacity and in most cases results in a less capital intensive system. The degree to which this is possible is a function of charging and discharging performance. The optimum system is one that establishes proper sizing of heat pump and storage in light of the energy use characteristics and capital cost resulting from each combination.

Providing heating storage with a leveling control generally does not allow a reduction of heat pump size relative to conventional operation. The heat pump must still be sized to meet the cooling load. However, storage does displace supplemental resistance heating. In the Boston area over 70 percent of the supplemental resistance heating was displaced when using the most cost effective system.

The full set of results indicates that in general, Configurations 1 and 2 are cost effective systems because of their performance characteristics and relatively low cost. Configurations 5 and 6 also offer advantages under certain conditions for these same reasons. Configuration 7 although offering technical problems during charging and discharging operation is the most cost effective heating storage configuration in most applications. Major factors which influence system costs such as storage material and TES subsystem design should of course be addressed in future work to improve the cost effectiveness of various systems. Significant accomplishments in these areas could alter the results presented here if these reductions in cost affect a particular configuration more than others. These initial results should be treated as preliminary until many of these design and operational changes are evaluated in the next three- to four-month period.

REFERENCES

[1] Sigmon, T. W., et al. "Simulation and Evaluation of Latent Heat Thermal Energy Storage Heat Pump Systems." Draft Task Report submitted to Department of Energy. Conducted under Contract DE-AC-01-79ET-26707, March 1981.

[2] Ferrell, G. C., et al. "Capital Cost Data for Thermal Energy Storage and HVAC Systems." Draft Report submitted to Department of Energy. Conducted under Contract Number DE-AC-01-79ET-26707, March 1981.

PROJECT SUMMARY

Title: Residential Scale Ice Storage System for Space Cooling

Principal Investigator: Harold H. Hopkinson

Organization:
Energy Systems Division
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Project Goals: Develop a commercially acceptable Residential Thermal Energy Cool Storage System for use with space cooling equipment in support of electric utility load management.

Conduct a marketing and economic study for Residential Thermal Energy Cool Storage Equipment.

Project Status: Negotiations were completed and a contract between Union Carbide and Carrier was signed during April 1981.

Work on Task 1 "Assessment of Prior Experience" started during May and is now complete. The report on this work was completed during August.

Work on Task 2 "Preliminary Conceptual Design" and Task 4 "Preliminary Economic Assessment" is in progress. Several system types are being considered for development. Computer programs have been revised to help select the most promising and cost effective ice bank system. Arrangements have been made for a customer side market study. It is planned to develop a questionnaire to obtain information from electric utilities for use in the utility rate study and economic evaluation. A marketing research consultant with utility experience will be utilized in the final preparation of this questionnaire.

Contract Number: 40X-92309C

Contract Period: April 1981 through November 1983

Funding Level: $259,615 (Phase I)

Funding Source: U.S. Department of Energy through Oak Ridge National Laboratory

RESIDENTIAL SCALE ICE STORAGE SYSTEM FOR SPACE COOLING

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ABSTRACT

Energy load management is fast becoming a necessity to electrical utilities. Thermal cool storage offers the utility a means of load management. The ice bank approach to thermal energy cool storage offers the most potential for development. Seasonal performance of both full and partial storage systems will be studied using a Carrier simulation program. These results will form the basis for selection of a system to be developed under this contract. Project work was started on Phase I during April 1981. The objectives of Phase I are the establishment of a conceptual design and completion of a marketing and economic study. Seasonal performance of the proposed equipment for several locations will be determined by computer simulation.

INTRODUCTION

Energy management techniques are rapidly becoming very important to electrical utilities. The Public Utilities Regulatory Policies Act (PURPA) and the National Energy Conservation Policy Act are examples of Federal mandates for energy management. The high cost of capacity expansion and utility fuels are another mandate. Improved operating efficiency through better utilization of available generating capacity is still another mandate for load management.

During the last few years, as more and more commercial and residential air conditioning units were added, many electric utilities have become summer peaking. Electrical loads resulting from air conditioning with its seasonal and daily variations cause poor system load factors. This trend has caused many utilities to consider some means of load management.

Thermal cool storage is one of the many methods which can help a utility to obtain an improved load factor. A thermal storage cooling system can reduce the peak power demand of an air conditioning system. The problem with equipment used in the past has been the poor efficiency, reliability and high cost of residential thermal cool storage equipment.

The goal for this project is to develop a commercially acceptable residential phase change thermal energy cool storage system for use with space cooling equipment in support of electric utility load management. The results will be plans and specifications for a reliable, low cost thermal cool storage system capable of meeting the established performance requirements.

DESCRIPTION

The proposed phase change thermal energy cool storage system to be developed under this contract is based on freezing ice on a submerged direct expansion evaporator. This system, while not the most efficient, is expected to be the most cost effective of all the possible alternatives. Simple, reliable, low cost equipment is of prime importance for residential installations. Ice harvesting schemes, while more efficient, require more expensive controls and evaporators. These systems are more suited to larger commercial systems where controls would not represent a large percentage of the total cost. Figure 1 is a diagram of the proposed static ice system. This system is similar to the experimental ice bank system Carrier has provided for field tests over the past few years. The ice bank unit is connected to a remote condensing unit and functions as a direct expansion evaporator. Refrigerant evaporates in the tubes immersed in the water tank, freezing ice on the tubes. Chilled water is pumped through the tank to melt the ice and to the indoor chilled water coil to provide space cooling. The condensing unit operates on a time programmed basis during off peak hours, making ice independently of the air conditioning demand. The circulating pump is activated by the air conditioning demand.

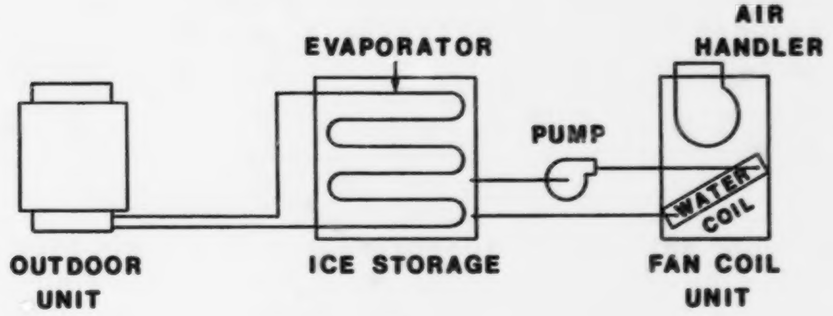

Figure 1. Static Ice System

The use of ice as a phase change material has many advantages and only one significant disadvantage, it freezes at 0°C (32°F) which is lower than necessary for air conditioning applications and tends to reduce the thermodynamic performance of the condensing unit. Some of the advantages of ice for a residential thermal storage system are listed below:

1. High thermal energy capacity
2. Availability and low cost
3. Non-toxic
4. Excellent and well known properties

Other important advantages of the proposed system are the need for only two heat transfer surfaces between the refrigerant in the evaporator and the conditioned space air, minimizing cycle losses due to heat exchanger temperature differences; the ability to operate the charging (freezing) system completely independent of the discharging (melting) system, avoiding complex controls; and the elimination of circulating pump operation during the charging cycle, minimizing auxiliary power consumption.

On balance, the ice bank approach offers the strongest potential for commercialization and early widespread use of thermal cool storage residential systems.

There are many methods of operating a thermal cool storage system. Probably the two most commonly known are: full storage and partial storage. Full storage freezes ice during off peak periods and melts ice to meet the building cooling requirements during the on peak periods. The condensing unit is sized to meet the entire load with operation restricted to only the off peak period. A partial storage system is sized to operate up to 24 hours a day in order to meet the daily space cooling load Ice is frozen during periods of low cooling demand and melted when the condensing unit capacity is less than the building load. Both of these systems and others must be analyzed to determine which will be developed under this contract.

An ice bank thermal energy storage system simulation program has been developed by Carrier to determine the relative seasonal performance for each of the proposed cool storage methods. For comparative purposes the performance of a conventional air conditioning unit can also be calculated using this program. A description of this program may be found in either of the two references listed at the end of this paper.

PROJECT DESCRIPTION AND PROGRESS

During April 1981 negotiations were completed and work was started on the residential thermal cool storage project. There are five basic tasks in each of the two phases of the contract. The Statement of Work is briefly outlined below.

Statement of Work

Phase I

Task 1. Assessment of prior experience
2. Preliminary conceptual design
3. Development (bench) testing
4. Preliminary economic assessment
5. Final report

Phase II

Task 1. Description of storage system
2. Developmental testing
3. Economic studies
4. Prototype design
5. Final report

The assessment of prior experience is complete. Work is proceeding on Tasks 2, 3 and 4 of Phase I.

The objective of Phase I is to establish the conceptual design and subsystem specifications for the thermal energy cool storage equipment to be developed under Phase II. The full or partial storage question has already been mentioned. Shall the equipment be designed for installation in new homes only or should it be for existing buildings or both? Can a standard condensing unit be used or must it be modified for thermal storage application? What is the range of system capacities required to meet the full range of home sizes throughout the U.S.A.? What should be the configuration and size of the prototype system to be developed under this project? These are just a few of the questions which must be answered during the Phase I work.

The cost effectiveness of the proposed thermal storage equipment will be determined by life cycle cost analysis. This involves a realistic determination of the most likely electrical rates to be applied to thermal storage equipment in the specific marketing geographic areas. Of the information necessary for an economic study, this is the most difficult to determine. It is also the most subject to change and error. This rate or range of rates used with the results of the annual system performance simulations enables calculation of the annual energy dollar savings - energy use will be greater - to a utility customer with thermal cool storage equipment. Other data, which must be determined or estimated for thermal storage equipment, is the first cost and annual service costs. The forecasted sales volume will depend on the ratio of dollar savings to equipment first cost. These calculations will also set the cost and performance goals for the prototype system to be developed under Phase II of this contract.

During Phase I, time has been reserved to make preliminary technical investigations of subsystems. Some of these investigations will involve actual laboratory tests while others will be paper studies. Load anticipation logic and control sensors as well as ice freezing evaporators will be reviewed in detail. Specifications for the cooling coil and the thermal storage tank will be developed. Storage tank construction and materials will be studied with a view towards improved performance and weight reduction.

The proposed prototype system will be modeled and annual performance simulations will be run for several selected geographic areas. This will provide the final input for the economic studies of Phase I.

Upon approval of the concept for a prototype thermal cool storage system, work on Phase II will begin. With the exception of an economic study update, Phase II work is confined to the development of plans and specifications for a specific prototype system.

SUMMARY

The prior experience which Carrier's various divisions have gained during the past few years through development and field testing of experimental ice bank units, as well as field monitoring of cool storage experiments, provides an extensive and unique background for this program. We are confident that the results will be an advanced residential cool storage system with the potential for early commercialization.

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PROJECT SUMMARY

Project Title: Evaluation of Olivine Ceramic Refractories for Thermal Energy Storage Applications

Principal Investigator: Hayne Palmour III, Billy M. Gay and Ronald L. Cochrane

Organization:
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Materials Engineering Department
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Project Goals: The principal objectives of this program are to (1) experimentally determine the degree of improvement in thermal and mechanical performance that can be obtained with an olivine thermal storage brick made of domestic materials using advanced processing techniques compared with state-of-the-art as represented by commercial European bricks, (2) conduct an assessment of existing German ceramic process technology and determine its adaptability to domestic raw materials and manufacturing practices, and (3) investigate, on a limited basis, methods for further improvement of domestic-olivine brick.

Project Status: This contract, in effect since 8/18/81, continues work initiated in January 1978, by the University and supported in part by the North Carolina Energy Institute from June 1978, through March 1980. Prior accomplishments of that program have been reported in two published papers, a Technical Report, and are summarized in the 1980 Proceedings of the DOE Thermal and Chemical Storage Annual Contractors' Review Meeting.

To date, under the present program, accomplishments include (1) installation of improved, computer-based instrumentation, (2) the use of this system to determine performance characteristics of a set of heat storage refractories under cyclic use conditions, (3) acquisition of the services of a knowledgeable European consultant, (4) continued lab-scale process/property optimization studies, and (5) comparative testing of olivine-based and magnesite-based heat storage refractories in the calorimetric test facility at Purdue University.

Future work includes (1) additional performance testing of heat storage refractories under cyclic use conditions, (2) additional lab-scale process/property optimization studies, (3) infrared mapping of heat loss from TES furnace in service, (4) accelerated thermal shock testing, (5) post-cyclic use evaluation of refractories, (6) wrap-up of assessment of existing German technology, and (7) publication of results.

Contract Number: US DOE Contract No. W-7405-eng-26, Union Carbide Corporation, Nuclear Division Subcontract No. 7959.

Contract Period: August 18, 1980 - November 30, 1981

Funding Level: $73,013.00

Funding Source: Department of Energy through Union Carbide Corporation, Nuclear Division (ORNL).

EVALUATION OF OLIVINE REFRACTORIES FOR TES

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ABSTRACT

High-heat capacity refractory ceramics have been employed in European electric heat storage furnaces for over two decades. In these systems, ceramic refractories are heated to approximately 1500°F, using low-cost electric energy during the off-peak demand hours. During the peak demand hours, heat is extracted as needed by controlled circulation of air through the core to meet space conditioning requirements. Heat storage or thermal energy storage (TES) furnaces represent (a) valuable load-leveling capabilities for electric utilities and (b) safe, convenient, reliable heat sources for consumers. Because of its relatively high-heat capacity and relatively low cost, olivine is one of the more attractive candidate materials for such ceramics. This paper includes a discussion of the goals of the current study, along with results achieved to date. Further, there is a discussion of future work to be undertaken as a part of this study.

INTRODUCTION

Investigations into the processing properties and performance of special refractory shapes produced from North Carolina olivine for prototype evaluations in heat storage furnaces began early in 1978, at North Carolina State University under the direction of Gay and Palmour. The primary objective of that initial work was to demonstrate the feasibility of using North Carolina olivine to make heat storage bricks of a quality equal to or better than their equivalent European counterparts. The results of that successful early work have been presented[1-5] and will not be repeated here. Additional research tasks are now being undertaken under U. S. Department of Energy sponsorship through Oak Ridge National Laboratory. They are directed toward more complete evaluation of the performance of University-produced olivine refractories for the central system furnaces being developed in the US from English-based designs, and toward similar evaluations of the German-style ceramics, also produced from North Carolina olivine, intended primarily for small, room-sized heat storage furnaces. Further laboratory-scale studies of optimization of properties and performance of olivine-based refractories will also continue. Additionally, a preliminary assessment of existing German technology in terms of its adaptability to domestic raw materials and manufacturing practices is being conducted.

The state of development and utilization of sensible heat storage systems in the US is still quite fluid. Decisions leading to substantial commitments to off-peak storage systems depend not only on favorable demonstrations of capability, performance and customer acceptance of such systems, but also upon favorable economics of the whole system, at all levels. Price and performance of the ceramic storage media influence the cost of the furnace to the consumer, which in turn influences the utility's thinking in setting off-peak rate structures to yield an appropriate investment payback period for the consumer.

All parties involved would like to have access to hard economic data at all levels in this multi-tiered system. Unfortunately, the truth is that no bonafide domestic heat storage ceramic refractories manufacturing capability exists in the US today. Our prior study and the current program have not been scaled so as to allow for a direct address of these economic issues. However, we clearly recognize their importance and, hopefully, our continuing efforts to characterize the technical performance and to improve processing and product quality can provide a sound technical basis, along with additional performance-related incentives, for undertaking further scale-up studies which will address the economic issues fully.

EXPERIMENTAL PROCEDURE

To accomplish the objectives of this program, a microcomputer-based, precision digital data acquisition/processing/recording system capable of handling up to 128 thermocouple (or other analog data) input channels and optional feedback control functions was acquired and installed. This system consists of a Kaye Scanner with 128 channels connected to thermocouples located at various places in the laboratory and with one thermocouple measuring exterior temperatures. One channel is connected to a watt-hour meter so that power input to the furnace can be monitored constantly. The output from the scanner is fed to an Apple II Plus, 48K microcomputer and stored on 5¼" floppy disks. The furnace in use is a TPI, Inc., OFF PEAK TM Comfort Conditioning Storage Equipment, Commercial Central (Model 21530) unit, rated at 30KW, but de-rated to 26.25KW because of limitations in electrical wiring in the laboratory. This does not alter the ability to reach the desired (and rated) temperature in the storage core, but rather, extends the time required to reach this temperature. It should be noted that our experience showed the storage core temperature always reached the desired maximum temperature within 8 hours. However, it should be pointed out that none of the cycles conducted thus far were during conditions of extremely low winter temperatures.

Figure 1 shows a schematic of the furnace storage core. Each small block represents a ceramic heat storage brick. There are 72 bricks shown in this figure and there are an additional 72 directly behind these, bringing the total in the storage core to 144 bricks. The numbers shown in Figure 1 correspond to the numbered thermocouples.

In placing the thermocouples, it was desirable to be able to record temperatures at the heating elements, in the center of the individual storage bricks and in the air channels. Considering the numbers in the blocks representing bricks, the numbers on the left represent thermocouples measuring element temperatures, the numbers in the center represent thermocouples measuring temperatures at the center of individual bricks (here after referred to as core temperatures) while the numbers on the right represent thermocouples measuring temperatures in the air channels adjacent to the brick (hereafter referred to as air temperatures). In each block having numbers, the bottom row of numbers represent thermocouples in (or adjacent to) the bricks in the front (those represented in the figure) while the top row of numbers represent thermocouples in (or adjacent to) the bricks in the rear (those directly behind those represented in the figure). For discussion purposes, the total bricks in each vertical setting (front and rear) are called a row while the total bricks in each horizontal setting (front and rear) are called a level. Rows are numbered from left-to-right while levels are numbered from bottom-to-top [example: thermocouple 161 is located at the element in row 1, level 1, in the rear; thermocouple 124 is located at the center of the brick (core in row 3, level 7, in the front].

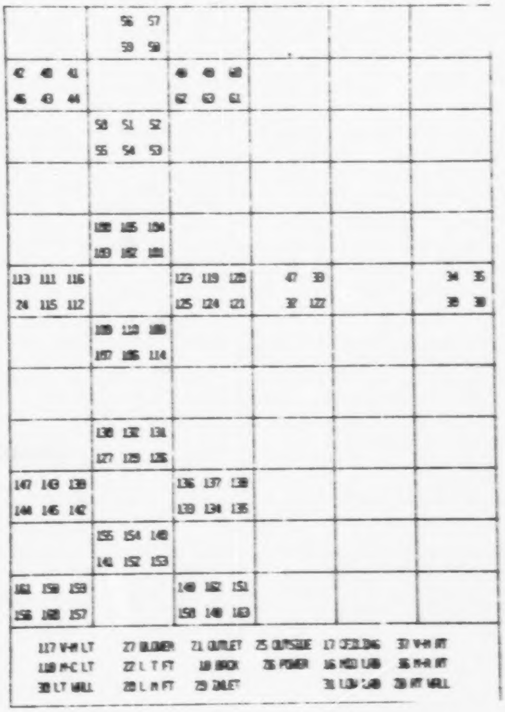


Figure 1. Schematic of Cer al Heat Storage Furnace storage core showing thermocouple locations.

The numbers in the large block at the bottom of Figure 1 represent thermocouples at locations outside the ceramic storage core. Thermocouples 18, 20, 22, 28 and 30 are cemented on the outer metal skin of the furnace; 18 in the center on the back, 20 in the middle of the left front, 22 at the top of the left front, 28 in the center of the right side and 30 in the center of the left side. Thermocouples 21, 27 and 29 are located in the plenums; 21 in the outlet plenum just behind the grill, 27 in the outlet plenum just in front of the blower and 29 in the inlet plenum. Thermocouple 25 measures the exterior temperatures. Position 26 is not a thermocouple; rather, it is the watt-hour meter input position. Thermocouples 16, 17 and 31 are at different vertical levels in the laboratory; 31 at 5' above the floor, 16 at approximately 12' above the floor and 17 just below the ceiling (~ 20' above the floor). Thermocouples 36, 37, 117 and 118 are at the interfaces between layers of insulation in the center of the sides of the furnace; 117 and 118 in the left side, 36, 37 in the right side.

Since the air is circulated up the channels in the front, over the top and down the channels in the rear, primary instrumentation was located in the left side of the furnace. It was assumed that the right side would closely approximate the left side in temperature distribution. Therefore, only 8 thermocouples were located in the right side to be able to check this assumption.

Primary studies of the German-style ceramics for room-sized heat storage furnaces were to be conducted at Purdue University in the calorimetric room test facility under the direction of Dr. Robert J. Schoenhals.[6-9]

RESULTS AND DISCUSSION

The primary objective for this program was divided into three components. The first was to determine the thermal and physical properties of the olivine thermal storage brick developed at N. C. State University (NCSU). This task was completed by the time this program was in place and has been reported previously.[3-5] The second part of this objective was to determine the effect of cycling on the mechanical stability of the NCSU brick. At this time there is no detectable degradation of the heat storage capacity and thermal conductivity as determined by temperature readings as a function of time and number of cycles, assuming that mechanical failure during cycling would result in a degradation of thermal properties. Further work is in progress and will be reported in detail later.

The third part of the primary objective was to determine the thermal gradients and temperature distributions in the brick storage core of a 30KW TPI heat storage furnace loaded with the NCSU brick and, again, when loaded with a commercially available European counterpart. The cyclic tests with the European bricks will begin in the early fall of this year and, obviously, results are not yet available. On the other hand, approximately 45 cycles have been completed with the NCSU brick and the data has been logged. Although the data from all the cycles was not recorded, nearly a million individual data points (i.e., temperature vs. time vs. position and power input vs. time vs. temperatures) were recorded. As reduction and analysis of this data has progressed, it has become apparent that the possible reduction schemes (and, hence, the usefulness of the data) are virtually limitless. The problem to date has been one of determining which reduction schemes will yield the most useful information. This has been complicated to some extent by the lack of input from others (i.e., furnace manufacturers, refractory producers, utilities, other researchers, etc.) to indicate what information would be most valuable to them. Additionally, the necessity of developing software and software routines as one proceeds slows progress on reduction and analysis of such a vast data base. Thus far these hurdles have been or are being overcome.

Because of the limited space available here, it is impossible to start to present all the data collected and then discuss it. Instead of attempting such a task, samples of the output will be presented to show typical temperature distributions and thermal gradients. This will be followed by a brief discussion.

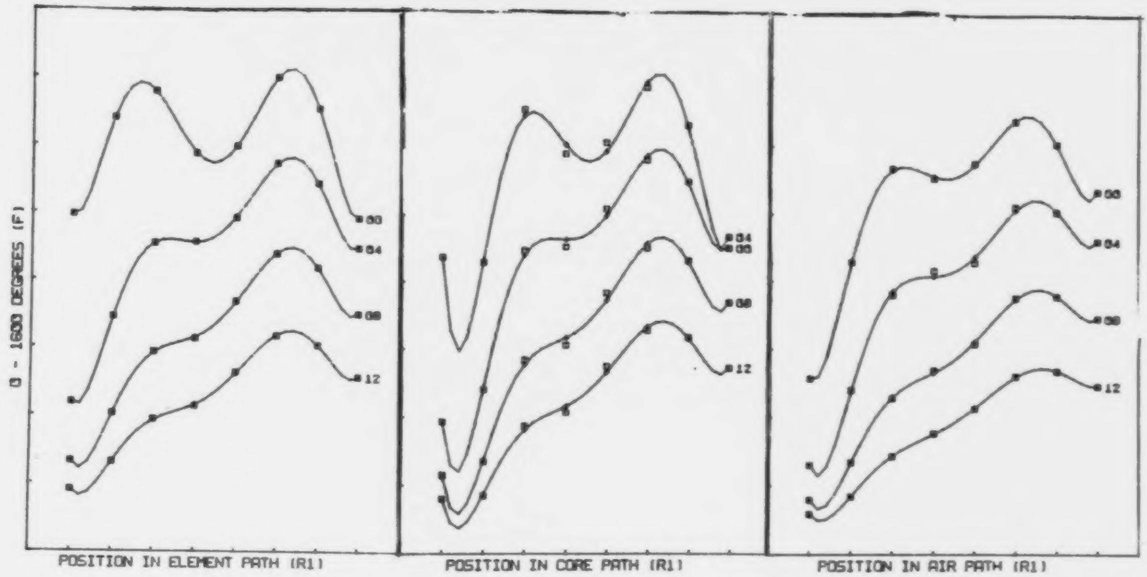
Figure 2 shows a series of curves representing temperature distributions in row 1 (R1). It should be pointed out that the temperature profile varies from row-to-row (and level-to-level, for that matter) because of the effects of thermal losses. Thus, one cannot look at one row and project that temperature distribution throughout the storage core. Rather, one must approach the whole storage core as a summation where rows 1 and 6, 2 and 5, and 3 and 4 are equivalent rows. This would be true for almost all data, not just temperature distributions.

In all three parts of Fig. 2, the positions correspond to different levels in row 1 (R1). Going from left-to-right represents going up the front, over the top and down the back (in the same manner as the air flow). Starting on the left, positions 1-4 are in the front at levels 1, 3, 7, and 11, respectively. Continuing to the right, positions 5-8 are in the rear at levels 11, 7, 3, and 1, respectively (see Fig. 1). The small squares represent actual data points. The curves were fitted using a sixth order polynominal of the form $x = a + by + cy^2 + dy^3 + - - -$. The +'s represent calculated points using the sixth order polynominal and the calculated coefficients. If all the curves fit the actual data perfectly, all the +'s would be inside the small squares.

In Fig. 2, the numbers to the right of the curves represent time, in hours, after the furnace blower was activated to start extraction of the stored heat. The temperature losses into the bottom plenum are indicated by the lower temperatures of level 1 (both front and rear) at the outset of discharge (represented by the end points of the curves for 0 hours. The temperature losses into the top plenum are represented by the lower temperatures for level 11 (both front and rear) shown by the minima in the center of the 0 hour curves.

The apparent drop in temperature between positions 1-2 and between positions 7-8 is due to the use of a sixth order polynominal, which tends to blow up at the boundaries (i.e., at level 1, front and rear), in these cases. Attempts to use a lower order polynominal to fit the data yielded curves which partially or, in some cases, totally lost the trends shown by the actual data points.

The curves in Fig. 2 are skewed to the left with increasing time, indicating that the heat stored in the front bricks is used first, as expected. It is interesting to note that ΔT for positions in the front of the furnace decrease with increasing times. Conversely, for element and core paths in the rear of the furnace, the ΔT for a given position increases with increasing time while the ΔT along the air path in the rear tends to remain essentially constant with increasing time. In the case of element and core paths, this indicates a greater dependence on the bricks in the rear to provide the heat



(a) (b) (c)

Fig. 2. Temperature profiles at various times within row 1 of the furnace storage core as a function of position: (a) Element temperatures, (b) core temperatures, and (c) air channel temperatures. Data collected on April 14, 1981.

necessary to heat the air. The relatively constant ΔT for the air path, in the rear, indicates that there is still sufficient stored heat to supply the systems heat demand, even after 12 hours of discharge. This also indicates the thermal conductivity of the bricks is sufficient to allow the stored heat to flow out to the air path. This can be seen even more clearly by comparing the air and core temperatures at positions 6, 7, and 8 for the 12 hour curves which show the core temperatures to be only 100-150°F greater than the air temperatures.

Another point of interest is the reheating which takes place in the rear of the furnace. This can be seen in Fig. 2(b) by comparing the 0 hour and 4 hour curves. In this case, a sufficient amount of heat has been transferred to the air so that as it reaches the bottom-rear, it is hotter than the bricks causing an excess temperature transferral to the bricks in this area.

When one considers rows 2 and 3 (not shown because of space limitations), he sees similar trends, but with the absolute temperatures increasing as he goes toward the center rows. However, the temperatures in the levels just above and below the plenums tend to stay fairly constant in all the rows. Another difference one sees for the center rows is that the temperature distribution curves for these rows tends to take on a smoother character with only one maxima and no true minima, especially with increasing time.

Rather than attempt to get into presenting other curves and discussing them, the remaining space will be spent discussing some of the other data reduction schemes and their output.

First of all, determination of thermal gradients within the storage core and through the insulation is well under way. At the moment, only gradients through the insulation and within a given brick can be output. However, one of the software schemes under development is a method for dumping all of the data to a mainframe computer which can handle it as one body of data instead of on the basis of one complete cycle. This will allow for developing whole storage core gradients, thermal mapping within the core, and many other possibilities.

Also under development is a scheme which will allow for determination of total energy input to the system and useful energy extracted from the system. Two different methods are being used to determine the amount of useful energy extracted from the system. One involves the use of average storage core temperature while the other involves using the total volume of air heated. The results of these two schemes will be compared and the more accurate will be used for final calculations.

As these analyses are conducted, and as the post cyclic evaluations of brick microstructure are completed, it is hoped that a microstructure to thermal performance relationship can be devised.

The comparative tests have been completed at Purdue University on the room-size storage systems. The results indicate very little difference between the magnesite- and olivine-based refractories in terms of total storage capacity and thermal conductivity. If there is a true and discernable difference, based on these results, one must say that the olivine-based refractories are superior.

FUTURE WORK

As has been indicated, work will continue in an effort to extract the most useful information from the current data base. Additionally, a similar, but not as extensive, data base will be developed for the European made counterpart to the NCSU brick. Post cyclic evaluations of the mechanical stability and microstructure will be conducted for both bricks.

Laboratory-scale opimization studies, including an accelerated thermal shock test will continue.

The input from the German consultant will be written up and published, jointly with him, in addition to forming the basis for a separate report under this program.

Additional studies will be conducted at Purdue University on the central storage system as well as on the room-size storage units. The comparative results of this work will form the basis for a jointly authored publication.

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PROJECT SUMMARY

Project Title: Alternatives to Ceramic Bricks and Ceramic Brick Systems

Principal Investigator: J. Michael MacDonald

Organization:
TRW
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Oak Ridge, Tennessee 37830

Project Goals: Characterize the properties of low-cost materials for use as TES media and the performance of associated electric storage furnace systems for customer-side-of-the-meter utility load leveling. Compare the proposed system costs and performance with state of the art electric storage furnaces. Identify appropriate system and materials research and development needs.

Project Status: The project is 85 percent complete, and preparation of the final report has begun. Low-cost, alternative materials were evaluated, including monolithic and loose-fill materials. Monolithic materials were ruled out due to cost. Several loose-fill candidate materials were identified and their properties established. A conceptual electric storage furnace system was developed to take advantage of using the loose-fill materials in a packed bed configuration.

An existing computer code at TRW for calculating one-dimensional temperature profiles of the gas and the solid in a packed bed TES system was modified and updated to allow the charging, discharging, and idle modes of operation of the proposed furnace system to be modeled. Existing research on heat transfer coefficients, pressure drops, and system modeling was reviewed, and appropriate information incorporated in the updated computer code. Numerous runs involving an eight hour charge period followed by 16 hours of alternating discharge and idle periods have been made. The performance of the packed bed furnace system has been established.

Fabrication and materials costs for the components of the proposed furnace system are being obtained from local manufacturers and suppliers. System components requiring further development have been identified. Research required for the advancement of this concept has also been identified.

With the limited data at this time, a significant cost advantage for the proposed system, with equivalent performance, over existing electric storage furnaces cannot be established.

Contract Number: 62B-13817C, Letter Release 62X-29

Contract Period: 12 January 1981 through 30 September 1981

Funding Level: $105,000

Funding Source: Oak Ridge National Laboratory

Alternatives to Ceramic Bricks and Ceramic Brick Systems

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ABSTRACT

Alternative materials for use as TES media in electric storage furnaces have been evaluated and selected. Selections were based on: low cost; availability; durability; and energy storage density. The materials selected were: taconite pellets; river gravel; crushed stone; and crushed (air-cooled) blast furnace slag. Essential material properties and energy storage densities were established. A conceptual design for an electric storage furnace using these low-cost materials has been developed. The performance of this conceptual furnace has been characterized by use of an analytical model. A computer code for the model has been developed. Existing performance data for present-day electric storage furnaces have been evaluated, and performance and design comparisons between present-day furnaces and the prototype furnace have been made. With the limited data at this time, a significant cost advantage for the proposed furnace, with equivalent performance, over existing electric storage furnaces cannot be established. Future work required for materials testing and component development has been identified.

INTRODUCTION

At this time, the primary TES media being considered for electric storage furnaces are special refractory (ceramic) brick-type shapes made of olivine or magnesite. These ceramic bricks are expensive - ranging from about \$3.25 to \$5.00 per brick depending on the source and availability (Ref. 1). Until recently, the major source for these bricks was from Europe, where this use of TES has existed for more than twenty years. Presently, commercial quantities of these bricks are not manufactured in this country; Tennessee Plastics, Inc. (TPI), Johnson City, Tennessee, manufactures limited quantities of olivine bricks but with no apparent price advantage. Magnesite is not available in this country except by expensive extraction from sea water. Only two siginficant deposits of olivine are known - one in North Carolina and one in Washington state. The locations of these mineral deposits present a potential problem of increased costs due to long transportation distances.

One of the goals of the U.S. Department of Energy (DOE) is to substantially reduce the use of premium fuels for electric power generation. Increasing the use of off-peak energy storage is one means of accomplishing this reduction. Since olivine bricks represent 30 to 40 percent of the cost of existing electric storage furnaces, and use of these devices is cost dependent, a reduction in furnace cost is important for increasing off-peak energy storage. For baseline comparison purposes, the mass produced price of a ceramic brick was assumed to be in the range of \$3.25 to \$5.00 per brick.

In this study, TRW is evaluating the performance, economics, and design considerations of TES systems which can serve as alternatives to the systems presently being considered for utility load leveling in customer-side-of-the-meter residential applications which employ ceramic bricks. The study was divided into two phases. The first phase was an evaluation of alternative materials. The second phase included conceptual design of a system using the alternative materials selected in the first phase and comparisons of the alternative system costs and performance with present-day electric storage furnaces.

ALTERNATIVE MATERIALS EVALUATION

The key criteria used in evaluating alternative materials as TES media were:

- Low cost
- Availability
- Durability
- Energy storage density

Other than substitute ceramic-type castings/extrusions, no monolithic materials were found which could be economically substituted for the olivine brick. Ceramic castings/extrusions were specifically covered under a separate research program and were not evaluated in detail for this study. Some of the promising candidates in this materials category include: fire clay bricks; alumina bricks; gypsum bricks; and taconite bricks.

Several loose fill materials were found which appear to be viable substitutes for the brick principle, the most promising of which were quartzitic river gravel and taconite pellets. Any reference to gravel in this paper will mean quartzitic river gravel. Both gravel and taconite pellets are durable and in a shape which prevents a phenomenon known as "racheting". River gravel is inexpensive and universally available. Taconite pellets possess a higher volumetric energy density. A TES system incorporating river gravel as a storage medium can be charged either by direct insertion of electric heating elements or by a flow of hot air. In the case of taconite, heating by direct insertion of electric heating elements may not be possible due to the low electrical resistivity of the medium.

The other loose fill materials identified were: crushed stone; crushed (air-cooled) blast furnace slag; and crushed scrap ceramics. Crushed stone includes many materials, and locally available materials will vary. For this report, crushed stone will mean granite, limestone, or dolomite. All other candidates were eliminated due to excessive costs, limited availability, and/or environmental hazards. Preliminary data indicates that scrap ceramic material will have limited availability. Of the remaining four candidates, each proved to possess excellent chemical, physical, and thermal properties. All four candidates were relatively inexpensive, with unit costs of \$3 to \$50 per ton, compared to \$390 to \$600 per ton for manufactured olivine bricks.

For a comparison of the projected storage media costs (material costs near the point of geographic availability), see Table 1. The storage cost is the projected cost of the thermal mass required to provide 750,000 Btu's (220 kWh) of storage when cycled between the ceiling temperature and 100°F. For convenience, data for olivine bricks are included to illustrate the magnitude of differences involved. As shown in Table 1, storage media exist which can be utilitzed at one-tenth to one-hundredth the cost of olivine bricks. A system analysis is required to determine the impact based on total system cost.

Table 1. Comparison of Storage Media

Material	Average Specific Heat (Btu/lb-°F)	Temperature Ceiling (°F)	Unit Cost (\$/ton)	Required Mass (lb)	Volume (FT^3)	Storage Cost (\$)
Olivine Bricks	0.23	1500	390-600	2400	17	470-720
Crushed Slag	0.25	1500	3-13	2100	28	4-14
Crushed Stone	0.25	1200	3-14	2700	30	4-20
Gravel	0.25	1200	3-14	2700	30	4-20
Taconite Pellets	0.20	1500	40-50	2600	18	50-63

Volumetric energy density is an important consideration because it is a direct measure of the size of the required "thermal store". Higher energy densities require less floor space and smaller containers, thereby providing both convenience and a more economical package. Assuming a packing factor of 0.60, the volumetric energy density of compacted crushed slag is 18 Btu/ft^3-°F; compacted crushed stone or gravel is 22 Btu/ft^3-°F; and compacted taconite pellets is 25 Btu/ft^3-°F. For comparison, olivine bricks have a packing factor of 0.87 and a volumetric energy density of 34 Btu/ft^3-°F. Crushed olivine ore was examined, and its performance is very similar to that shown for crushed slag. However, at \$30 per ton, it was not included as one of the top four candidates. Except for crushed stone - dolomite and limestone in particular, which begin to decompose to lime (CaO) above 1,350°F - all the materials may be able to operate in a 1,500°F temperature regime. Testing is required to determine a suitable temperature range for each material. The relationship between storage temperature and volume is shown in Figure 1.

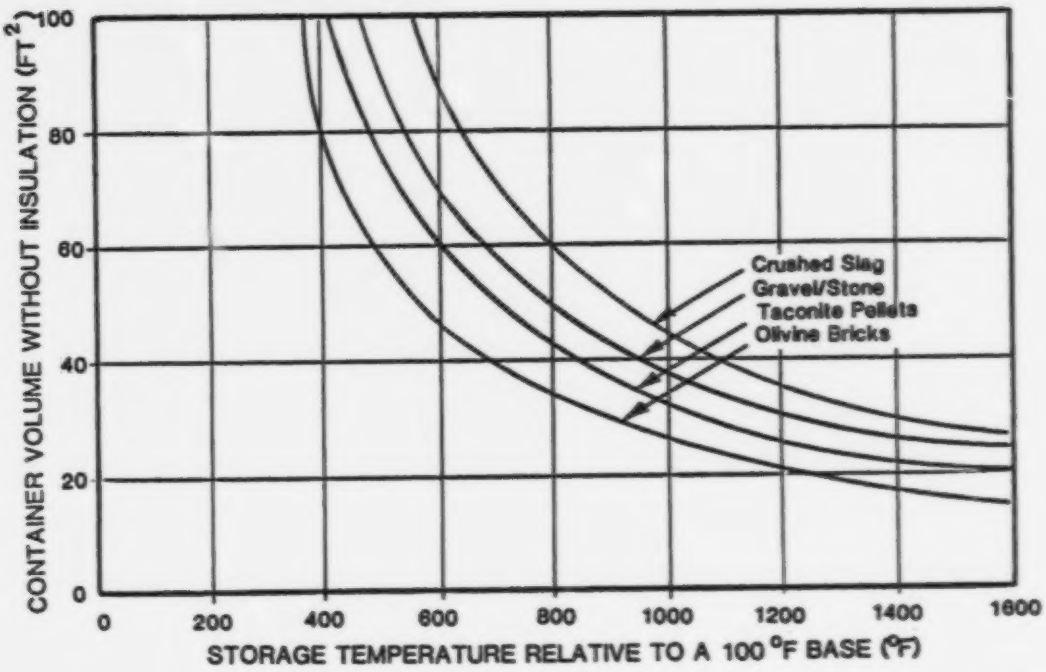

Figure 1. Thermal Storage Volume Requirements for Storing 220 kWh

Of the alternative materials, the volumetric energy density of gravel and stone is second only to taconite pellets; regarding cost and availability, gravel is second to none. Gravel is available over the entire U.S. Washed and screened gravel and sand are the largest dollar volume mineral in the U.S. Washed and screened gravel is available in any size and distribution of sizes.

Transportation quickly escalates the delivered price of a commodity which has a low unit cost. Both crushed slag and taconite pellets are very limited in terms of their availability. The availability of crushed slag is limited to iron and steel production regions of the country and the availability of taconite pellets is limited to those regions of the country involved in the production of iron ore. However, crushed stone is produced in every state except Delaware and North Dakota, and gravel is produced in every state of the country making it virtually a universal commodity.

Regarding thermal cycling, virtually no data exists for the materials investigated in the upper temperature ranges of concern for this TES application. Until this time, there has been no need to know how gravel, crushed stone, crushed slag, and taconite behave in a fluctuating temperature environment of 100-1500°F. Therefore, a testing program is recommended to determine precisely the temperature range in which each material could satisfactorily operate. Preliminary testing results from Pacific Northwest Labs (PNL - Battelle Northwest) indicate that problems may be encountered with taconite. The pellets have not held up well, and free hydrogen gas is being generated at higher temperatures (possibly due to free iron in the pellets stripping oxygen off water vapor in the air). However, the requirements at PNL, using compressed air, are different than those for the present system. Air cooled slag is known to produce hydrogen sulfide gas upon initial heating. Therefore, this material should require initial heating to drive off this noxious gas.

STORAGE FURNACE BASELINE

The 30 kW electric storage furnace manufactured by TPI was used as the baseline unit for comparison in this study. Independent testing of this unit is proceeding at Purdue University (Herrick Labs.), and some test results were presented at last year's meeting (Ref. 2). During a typical cycle, 172 kWh of energy are recovered with an input of about 240 kWh. The residual energy is 39 kWh, which leaves 29 kWh to account for thermal losses. The 172 kWh is recovered over about 16 hours. Assuming a temperature difference equal to 130°F minus 70°F or 60°F, the calculated average (house) air flow rate is 570 SCFM. No information is available on intermittent operation (i.e., alternate discharging and idle periods).

ALTERNATIVE CONCEPTUAL DESIGNS

One advantage of using loose fill materials from a heat transfer standpoint is that these materials represent a packed bed storage system. Temperature fronts in such a system should move in a reasonably uniform manner up and down the bed when the air flow rate is sufficiently high. An external heating system was selected over an internal one: 1) to minimize localized, elevated heat flux rates experienced by the TES medium (which should allow higher temperatures); 2) to eliminate problems caused by the electrical conductivity of the bed (e.g., taconite); and 3) to simplify control for partially charging the bed to a timing function with simple temperature overrides instead of a position function. This configuration also makes counterflow operation possible, which should be a significant advantage for partially charging the bed on other than peak days.

Some installation constraints were established. The unit was limited to a height of six feet and a width of two feet to allow maneuvering through doors and in tight places. Access panels or ports must be provided for filling and emptying the loose fill TES medium. Special consideration is required of some components. The reversible fan will be of a special design. The fan blade and shaft can expect to experience temperatures of 700-800°F for an hour or less. These temperatures will necessitate an extended shaft, special bearings, and thermal isolation of the fan shaft and motor shaft. A direct drive is still preferable. Fortunately, motor size is small - one-tenth horsepower or less. Since pressure drops of 1 inch water columns or slightly more have been calculated for the fully charged condition, the fan should be of tube axial design. An inner metal shell appears necessary to channel hot air flow through the TES medium. A cost advantage may be obtained by lining mild steel with rigid refractory insulation (13-15 lb/ft^3) to avoid using stainless steel for this item. Regarding strength requirements, the assumption of hydrostatic conditions yields a 6 psi stress at the bottom of the container. Reasonable dimensions for the inner shell (66" high by 54" x 18") were used to determine some of the parameters for the proposed system. An outer appliance cabinet is required to protect the insulation. The air flow openings should be equivalent to a nine inch diameter to accomodate an air flow of 115 SCFM. An opening of 18" x 4" is reasonable. The 30 kW air heater would be designed to heat 95 SCFM from 70°F to about 1000°F. The actual flow rate would vary from 95-115 SCFM with a constant speed fan, depending on the temperature profile in the packed bed.

A schematic representation of the resulting system is shown in Figure 2. A flow rate of 100 SCFM during discharging would allow a mixed air tempertaure of greater than 140°F immediately after charging with a whole house flow rate of 1200 SCFM. During intermittent operation, this drops to 130°F one hour after the charge cycle ends due to thermal losses.

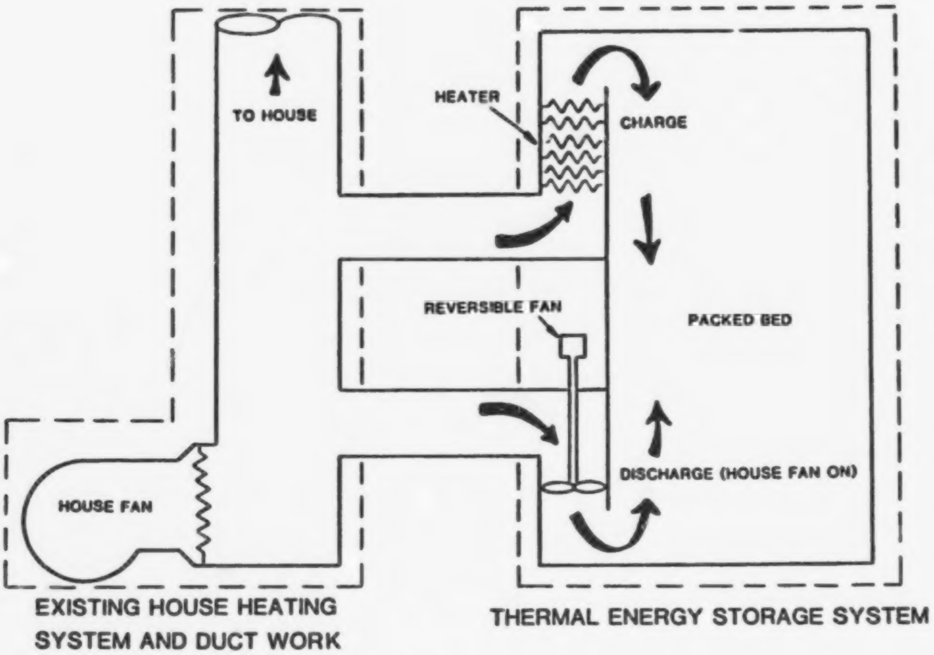

Figure 2. Packed Bed TES Furnace Schematic

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ANALYTICAL MODEL DESCRIPTION

To determine the performance of the alternative system, a method of modeling energy exchange within the packed bed, pressure drops, and losses to the ambient was required. Temperature profiles within the bed and of the air flowing through the bed were also desired. A model was developed and implemented as a computer program. The model is a finite difference model which uses the decoupling approach suggested by Hughes (Ref. 3). A predictor-corrector algorithm was used which matched the Schumann curves developed by Mumma and Marvin (Ref. 4) very closely when using their data. The model allows air flow reversal for charging and discharging and calculates the pressure drop and air flow rates assuming a constant speed fan is used. The model allows an arbitrary schedule of charge, discharge, and idle periods and calculates expected surface temperatures and the location of the hot spot.

SYSTEM ANALYSIS AND COMPARISON

The dimensions of the loose fill TES medium containment were selected as 66" by 54" by 18", for a total medium volume of about $37 ft^3$. The volume of bricks in the TPI 30 kW unit is a little more than 16 ft^3. For the purposes of this study, the inlet air temperature was limited to 1000°F. The behavior of these alternative materials is uncertain at higher temperatures, and in the absence of specific test data, a temperature below the potential upper limit was used. This choice increased the storage volume required. Further simulations at higher temperatures are planned. The bulk packing densities used were 90 lb/ft^3 for gravel or stone and 143 lb/ft^3 for taconite (taconite data were from Hanna Mining Company, Cleveland, Ohio).

For the dimensions and upper temperature chosen for the alternative system, the rocks were able to store 210 kWh and taconite stored 220 kWh. The total electrical inputs, including losses, were 221 kWh and 232 kWh, respectively, during the eight hour charging cycle. During tests at Herrick Labs, the TPI unit has been observed to charge 210 kWh over eight hours, with charging to 235 kWh taking about nine hours. The TPI unit has been charging at less than 30 kW at Purdue. For the comparison presented here, the effective average (house) air flow rate of 570 SCFM was corrected to 510 SCFM to account for this difference. This flow rate was used to calculate the mixed air temperatures shown in Figure 3. The inlet air temperature is 70°F.

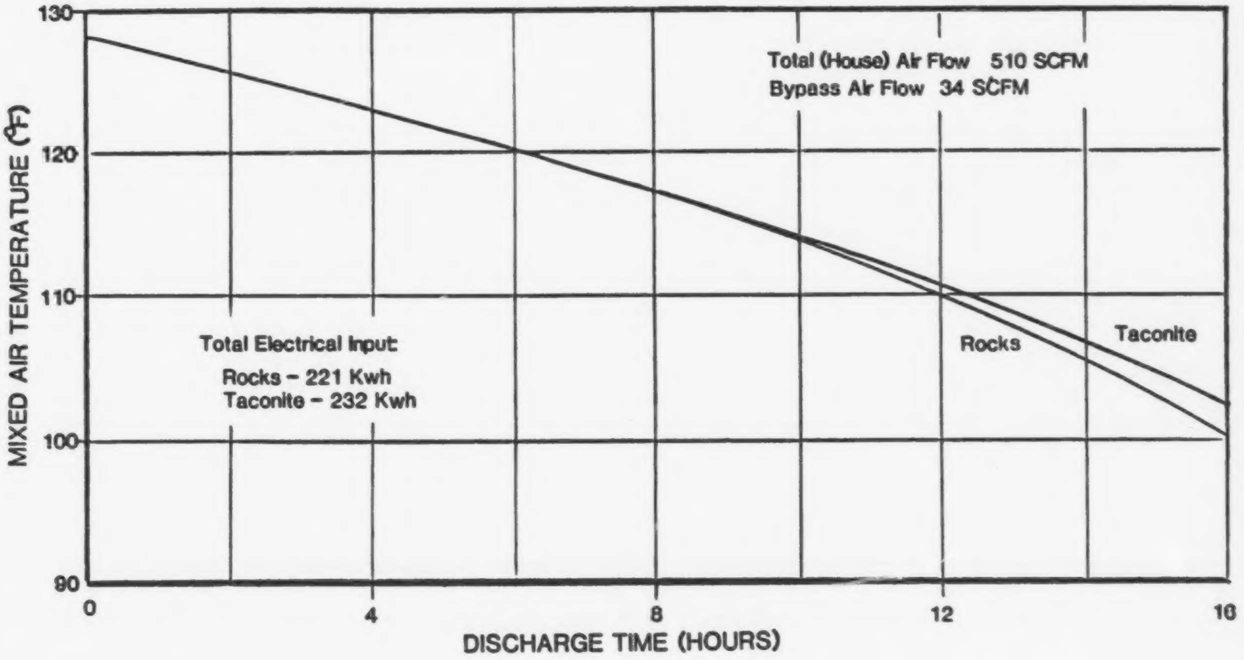

Figure 3. Discharge Air Temperature Profiles for the Alternative TES System

One criterion used in Standard 94.2P of the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) for electrically heated TES devices is that after the outlet temperature has fallen one fourth of the difference between setpoint and inlet temperature, the discharge cycle is stopped. For the alternative system shown here, this procedure would leave a residual charge of 100 kWh for taconite and 85 kWh for gravel/stone when the inlet temperature is 70°F and the setpoint is 128°F. This proposed criterion does not appear useful from the standpoint of recovering the most energy possible. The residual energy of the TPI unit is calculated subject to this constraint also. For purposes of comparison, the data for the TPI unit have been modified to reflect a total charge of 210 kWh and the estimated lower residual energy if the outlet temperature drops below the ASHRAE 94.2P limit. The comparison is shown in Table 2. Note that since the columns cover different time periods, the values are not additive.

Table 2. Performance Comparison

	Energy Stored (kWh after 8 hours)	Energy Recovered (kWh for 16 hours)	Residual Energy (kWh)	Energy Losses (kWh after 24 hours)
Proposed System				
Rocks	210	159	30	32
Taconite	222	157	46	30
TPI System	210	160	30	27

The TPI system should be capable of storing 235 kWh of thermal energy over about eight hours, and the proposed system is inherently limited to less than 100 percent charged. (For the cases shown, about 85 percent of full charge is achieved.) While the comparison may seem unfair, the intent is to show that simulations of the proposed system indicate good potential performance.

From a practical standpoint, the proposed system was designed to operate with an intermittent (house) air flow rate of 1200 SCFM, and the low flow rate used for the tests at Herrick Labs would lead to such low flow rates through the packed bed that uniform flow would be unlikely (Ref. 5).

The proposed system is especially valuable for those utilities which have shorter charging "windows" during the day, since a portion of the bed is inherently charged to near maximum temperatures in shorter time periods - 20 percent of the bed can be brought to 800°F-1000°F in about two hours. Energy can also be recovered at these high temperatures.

The proposed system is larger than the TPI unit. The expected "footprint" of the proposed unit is about 12 ft^2, while the unit stands six feet high. The basic TPI unit occupies about 9 ft^2. Regarding costs, no firm comparisons can be made, but the cost to a manufacturer for producing units which can only be charged to 1000°F appears to be $1300-$1400 in limited quantities. A markup of $500-$600 per unit would put the price in the range currently charged by TPI. In addition, significant certification costs could be expected. Additional simulations are planned to determine cost reduction potential for increased temperature limits.

In conclusion, the proposed system warrants further study as an electric storage furnace of the future. Smaller units, for utilities with low demand "windows" during the peak demand periods are a possibility. Significant component development work is required. Testing of the alternative materials to determine their performance in a tall packed bed at higher temperatures is required. In the case of air cooled slag, initial firing is necessary to eliminate hydrogen sulfide gas. Also, preliminary testing results from Pacific Northwest Labs (PNL - Battelle Northwest) indicate that taconite pellets may not held up well, and free hydrogen gas may be generated at higher temperatures.

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PROJECT SUMMARY

Project Title:	Thermal Energy Storage Testing Facility
Principal Investigator:	Robert J. Schoenhals
Organization:	Ray W. Herrick Laboratories School of Mechanical Engineering Purdue University West Lafayette, Indiana 47907
Project Goals:	Develop and evaluate apparatus and test procedures for establishing thermal performance of electrically heated thermal energy storage (TES) units. Provide technical information to assist ASHRAE in its effort to establish a standard for this purpose. Obtain test results for evaluating performance associated with particular TES unit configurations and energy storage materials.
Project Status:	A calorimeter chamber has been designed, constructed and instrumented. Improvements in the apparatus and in the test procedures have been incorporated in order to yield test results of acceptable quality, as determined in accordance with an overall energy balance and also an error analysis. Seven different room-size TES units have been tested using this facility. A study of the radiative and convective heat transfer contributions to the total thermal output of a unit during testing has been conducted. Test results have also been used to compare the performance of olivine energy storage bricks with that of magnesite bricks for two TES units. Laboratory apparatus and procedures for testing of central TES units have been evaluated and improved. A 30 kW central TES unit has been tested in a typical laboratory environment and also in an environmentally-controlled room in order to determine the influence of ambient air temperature and humidity variations on the test results. In addition, test results have been used to compare the performance of domestic olivine energy storage bricks with that of the English-manufactured olivine bricks currently supplied for this particular central TES unit.
Contract Number:	W-7405-eng-26 (ORNL/Sub-7961)
Contract Period:	November 1, 1980 through February 28, 1982
Funding Level:	$89,255
Funding Source:	Union Carbide Corporation, Nuclear Division

THERMAL ENERGY STORAGE TESTING FACILITY*

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ABSTRACT

Development of a prototype testing facility for performance evaluation of electrically heated thermal energy storage units is being pursued. Laboratory apparatus and test procedures are being evaluated by means of measurements and analysis. Testing procedures have been improved, and test results have been acquired for commercially available units. A 30 KW central unit and several smaller individual room-size units have been tested. This work is associated with a parallel effort by ASHRAE to establish a standard for performance evaluation of units of this type.

INTRODUCTION

In this project experiments and analysis are being pursued using electrically heated thermal energy storage (TES) units. In these devices high heat capacity ceramic bricks are employed as the energy storage medium. Large central units are currently available for replacing conventional residential furnaces. Also on the market are small self-contained room-size units which avoid the necessity for ductwork and a central air handling system. Energy charging of these devices occurs at night using less expensive off-peak electrical energy. During this period the electrical heaters inside a TES unit are activated, heating the ceramic bricks to a high temperature. Air is then caused to flow over the bricks intermittently throughout the day and evening as required to maintain the residence air temperature. The air flowing over the bricks is heated during this process, and the bricks are correspondingly cooled. Their temperature level is eventually lowered substantially, thus permitting another energy charge during the next night-time period.

This project is associated with a parallel effort by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) to establish a standard for performance evaluation of electrically heated TES units. Such a standard is now needed in view of the recent increase in marketing of these units within the U.S. Since electrically heated TES units have been in widespread use in Europe for many years, a German Standard, DIN 44572 (reference 1), has been established. This standard has been useful in guiding the more recent effort in the U.S. In regard to this effort, ASHRAE Proposed Standard 94.2P was released in December 1979 (reference 2). This document has been revised, and is expected to be released again in the near future. Brief accounts of earlier activities pursued in this project are given in references 3 and 4. Portions of the descriptive material given in this paper were taken directly from reference 4.

Certain advantages are obtained by testing the smaller room-size units inside a calibrated calorimeter chamber. Central TES units, on the other hand, are tested in a typical laboratory environment. Detailed accounts of the initial work on these two types of tests are given in references 5 and 6. The remainder of the paper describes test apparatus, procedures and recent results obtained.

TESTING OF ROOM-SIZE TES UNITS

The method used for testing of room-size TES units is illustrated in Fig. 1. Figure 1(a) shows the TES unit within the calorimeter chamber and the pertinent energy flow rates. Figure 1(b) contains a calibration chart generated experimentally under steady state conditions prior to testing. Figures 1(c) and 1(d) contain typical test results obtained with a 2 KW TES unit during a dynamic discharge test (internal fan within the TES unit turned on after the unit is fully charged). Employing the measured inlet to outlet air temperature difference and the calibration chart shown in Fig.1(b), a plot of the thermal output rate of the unit was generated [Fig. 1(c)]. Notice that the thermal output rate rose abruptly when the internal fan was turned on. By integrating the thermal output rate curve of Fig. 1(c) the thermal energy delivered by the TES unit was obtained, as shown in Fig. 1(d). The upper curve in Fig. 1(d) represents the electrical input energy, which was delivered to the TES unit at a constant rate for approximately 7 hours and then terminated. At any time the difference between the electrical input energy and the thermal output energy represents the energy stored within the unit. This is also shown in Fig. 1(d). Notice that the total energy output of the TES unit over the

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* This project is supported by Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, under Contract No. W-7405-eng-26 (ORNL/Sub-7961).

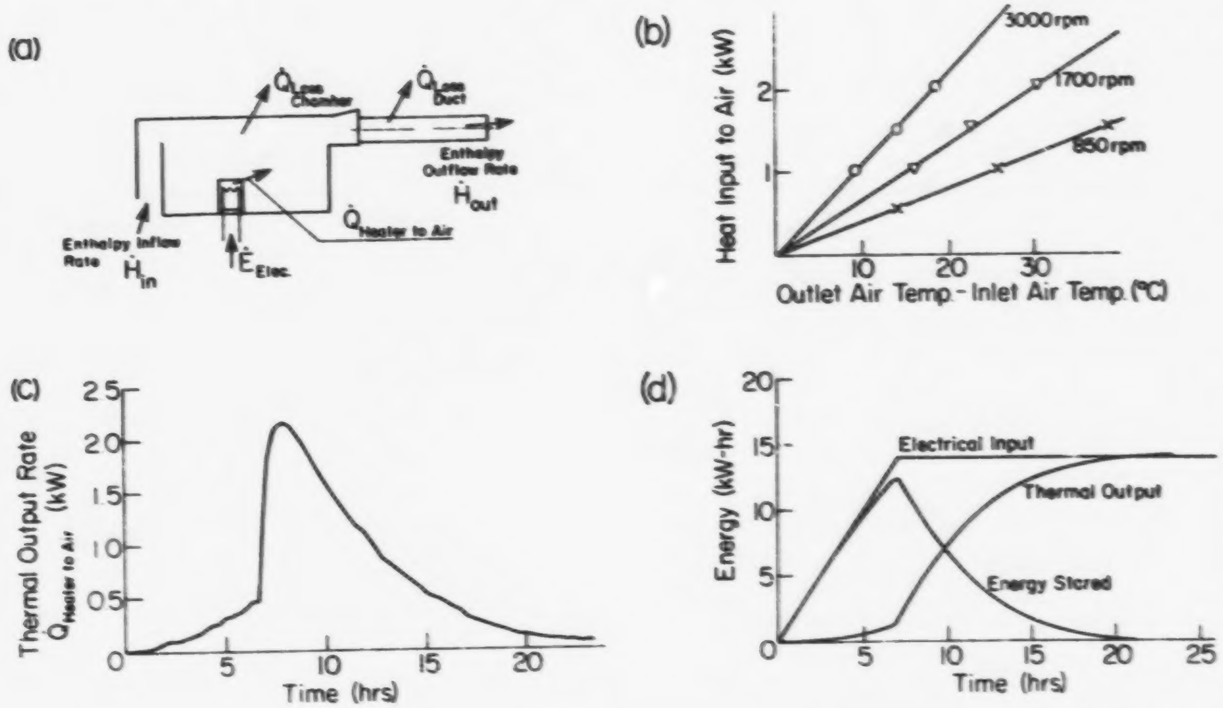

Fig. 1. Testing of Room-Size TES Units: (a) Schematic Diagram of the Essential Features of the Calorimeter Chamber Illustrating the Various Energy Flow Rates, (b) Calibration Chart Obtained Under Steady-State Conditions with Calorimeter Blower Speed as Parameter, (c) Thermal Output Rate During a Dynamic Discharge Test of a 2 kW TES Unit [Calorimeter Blower Speed = 850 rpm], (d) Energy Graph Associated with the Test Corresponding to (c).

extended duration of the test was essentially equal to the total electrical energy input, as expected.

During the past year 7 different TES units marketed by 4 different manufacturers ranging in size from 2 KW to 6 KW (based on the rate of electrical input) have been tested in the calorimeter using several alternate procedures. Experience gained from these tests has provided a means for evaluating the quality of the experimental apparatus, procedures and test results. The method of testing assumes the thermal inertia of the air within the calorimeter and the calorimeter walls to be negligible since the steady state calibration is applied under transient conditions during testing. This assumption was verified by including these effects in the processing of experimental measurements (reference 7). Another study was performed to determine the heat losses due to radiation during testing (reference 7). Figure 2 shows the heat output of a 2 KW TES unit during a dynamic discharge test and the estimated radiative and con-

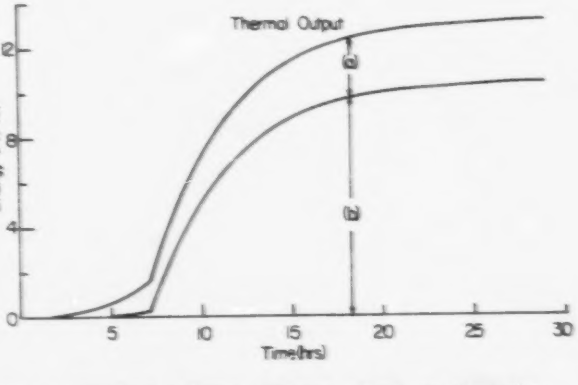

Fig. 2. Thermal Output Energy from a Dynamic Discharge Test of a 2 kW TES Unit and Estimated Contributions due to (a) Radiative Heat Transfer and (b) Convective Heat Transfer Based on Temperature Measurements.

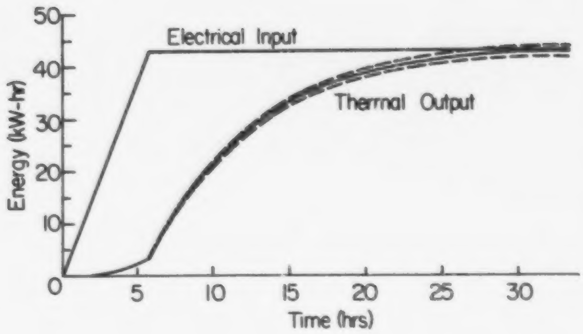

Fig. 3. Measured Input Energy and Calculated Thermal Output Energy for a Dynamic Discharge Test of a 6 kW TES Unit. [Estimated error bounds for the output are based on a 95% confidence interval.]

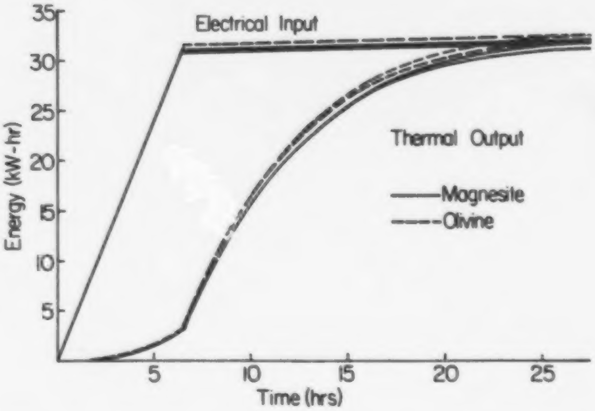

Fig. 4. Comparison of Performance of Olivine Bricks with that of Magnesite Bricks Based on Dynamic Discharge Tests of a 4 kW TES Unit [2 tests for each case].

vective heat transfer components based on temperature measurements. Figure 3 shows the results of a dynamic discharge test and also the estimated range of error. The calculated total thermal energy output of the unit possesses an estimated error of approximately ± 2.5% at the end of the test. This agrees with testing experience. It has typically been found that the calculated thermal output is within 2.5% of the measured electrical input energy. Figure 4 shows a comparison of the performance of a 4 KW TES unit containing domestic olivine bricks (reference 8) with its performance when containing the conventional magnesite bricks supplied by the manufacturer. Both sets of curves were obtained from dynamic discharge tests. Similar results were obtained with a 2 KW TES unit. Although the thermal properties of the two types of bricks are somewhat different, the differences in thermal performance are small. The reasons for these small differences in performance are still under study. Additional items investigated during the past year include the effects of the choice of calorimeter blower speed, setting of dampers, ambient air temperature variations, and cycling at the end of the energy charge period.

TESTING OF CENTRAL TES UNITS

In contrast to the room size TES units which are tested in a calorimeter chamber, proposed procedures for performance evaluation of central TES units involve testing in a typical laboratory environment. Figure 5(a) contains a diagram illustrating the configuration recommended by ASHRAE Standard 94.2P. Utilizing measurements of air flow rate and the inlet to outlet air temperature difference, the thermal output, residual capacity (energy stored at the end of each nominal discharge period) and heat loss from the cabinet can be displayed along with the measured electrical energy input on an energy graph as shown in Figure 5(b). A 30 KW central TES unit was used in conducting this dynamic discharge test. The unit was charged, discharged, recharged, discharged and then recharged, according to ASHRAE Standard 94.2P. A second type of test, called the maximum standby emission test, is used to determine the heat loss from the cabinet when the unit is fully charged and with the internal fan off.

Early tests were conducted in the laboratory according to the procedures discussed above. On the basis of the conditions recorded during testing and also the test results obtained, questions arose with regard to the possible effects of the ambient air temperature and humidity levels, and air temperature variations occurring during the tests. In order to evaluate these effects the 30 KW central TES unit was installed inside an environmentally-controlled room for further testing. Figure 6 shows the energy curves obtained from dynamic discharge tests conducted at 3 different ambient air temperatures. All 3 tests were performed at maximum fan speed and employing an outlet air set point temperature of 54.4°C (130°F). The deviations among the energy curves are the result of the various inlet-to-outlet air temperature differences that occurred when the inlet air temperature level (ambient air temperature level) was varied from 10 to 30°C. The calculated thermal output based on test measurements accounting for the effect of air humidity was compared with the corresponding calculated thermal output utilizing the thermal properties of dry air. This comparison was made for several dynamic discharge tests, and the deviations between the two sets of results were found to be only 1/2% or less. It is therefore concluded that it is not essential to account for air humidity in the processing of test measurements. Dynamic discharge tests of the central TES unit were also conducted with

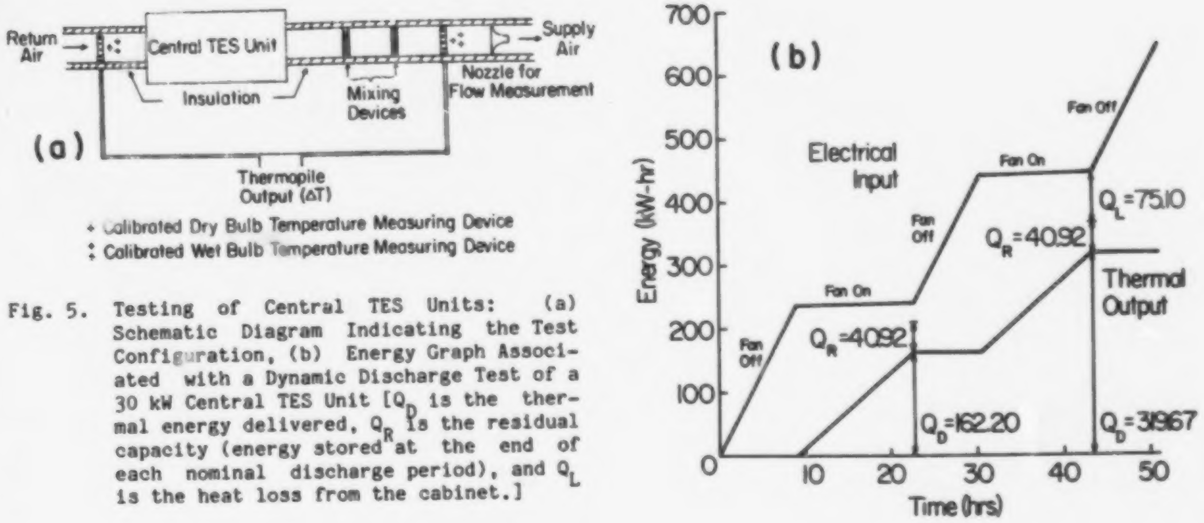

Fig. 5. Testing of Central TES Units: (a) Schematic Diagram Indicating the Test Configuration, (b) Energy Graph Associated with a Dynamic Discharge Test of a 30 kW Central TES Unit [Q_D is the thermal energy delivered, Q_R is the residual capacity (energy stored at the end of each nominal discharge period), and Q_L is the heat loss from the cabinet.]

the conventional bricks supplied by the manufacturer replaced by domestic olivine bricks (reference 8). The resulting energy graphs were found to compare quite closely with those obtained employing the conventional bricks supplied by the manufacturer (produced in England). Although the ambient air temperature was found to have an appreciable influence on results obtained from dynamic discharge tests (Fig. 6), results from several maximum standby emission tests revealed that ambient air temperature variations from 10 to 30°C produced no significant changes in the rate of heat loss from the TES unit to the ambient air.

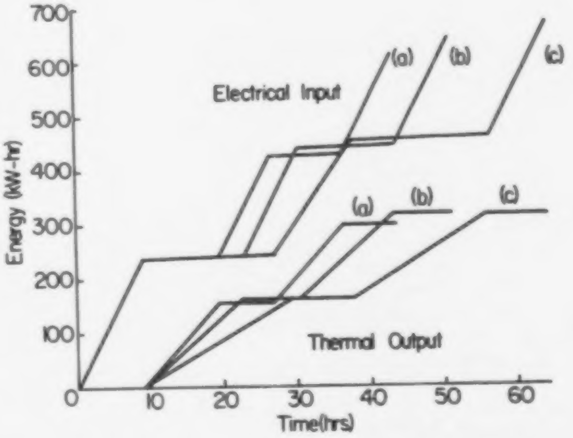

Fig. 6. Energy Curves Obtained from Dynamic Discharge Tests of a 30 kW Central TES Unit with a Set Point Temperature of 54.4°C (130°F) and Ambient Air Temperatures of (a) 10°C, (b) 20°C and (c) 30°C.

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PROJECT SUMMARY

Project Title: Field Evaluation and Assessment of Thermal Energy Storage for Residential Space Heating

Principal Investigator: H.N. Hersh

Organization:
Argonne National Laboratory
Special Projects Group
Argonne, IL 60439

Project Goals: Experimentally determine the technical performance of commercially available TES residential heating units under severe U.S. weather conditions. Assess the benefits and costs of TES to the customer, the utility and society. Determine user acceptance of TES. Identify and define TES issues, R&D needs and barriers to commercialization. Establish optimal sizing procedures.

Project Status: A data base has been developed based on two heating seasons and 45 test and 30 control homes in Maine and Vermont. Based on first analysis of monitored temperatures and electrical energy used for space heating, fuel bills and reports of users and utilities, the technical performance of TES ceramic and hydronic systems is deemed to be technically satisfactory and there is a high degree of customer acceptance and positive attitudes towards TES.

Analysis of house data shows a high degree of variability in electric heat energy demand for a given degree-day.

An analysis is underway to investigate relative differences in the efficiency of electricity utilization of storage and direct heating devices.

The much higher price of storage systems relative to direct systems is an impediment to market penetration.

A changing picture of rate structures may encourage direct systems at the expense of storage systems.

Contract Number: 19Y-69761

Contract Period: April 1, 1981 through December 31, 1981

Funding Level: $64,000

Funding Source: U.S. Department of Energy, through Oak Ridge National Laboratory

Field Evaluation and Assessment of Thermal Energy Storage for Residential Space Heating: An Interim Report

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1 ABSTRACT

Based on New England field test data covering two heating seasons, TES is technically viable and acceptable to its users. An analysis is underway comparing the efficiency of electricity utilization of direct and storage heating systems. Economics (higher cost of TES systems and changes in rate structures) represents the largest impediment to sufficient market penetration.

2 INTRODUCTION

In earlier work, field studies in Vermont and Maine were carried out to evaluate the performance of TES systems. The experiment involved 45 TES-heated homes; 30 electric baseboard-heated homes served as controls. Monitoring equipment recorded the electric heating demand and the inside and outside temperatures every 15 minutes in each home. All of the participating homes had been energy-audited by the local electric utility company. Most of the TES units in the test homes were room-type ceramic storage heaters, but six hydronic storage heaters and one central ceramic storage furnace were also being tested. All units were sized by the vendor to meet the full design-day heating load and were commercially installed.

It was determined that properly sized TES space heaters provide heating comfort, and it was concluded that properly designed off-peak electric rates can provide operating economies to the user. In that performance period not all of the data could be analyzed, and some questions and uncertainties had arisen with respect to its energy conservation potential, the use patterns of TES compared to direct systems, Rand D needs, the attitudes and complete satisfaction of users, its true-cost-effectiveness and its potential marketability. The following is a report of ongoing work to carry this study to completion, and touches on technical and economic considerations that can affect market penetration.

3 FINDINGS

3.1 TECHNICAL

Performance. Overall performance of the TES systems is good if properly sized for the home, and used properly. The major criterion for this assessment was the maintenance of essentially identical inside temperatures in thermally matched test and control homes throughout the heating season, e.g., on typical January days, on October days (which have more volatile temperature fluctuations), and on the coldest day of the year. In Vermont the lowest temperature recorded at the sites was -28°F on February 12, 1979; in Maine 70 degree-days were accumulated on February 14 of that year, providing rare opportunities to observe heating-system performance under design conditions and to evaluate shortcomings in sizing. Graphical records of daily electrical demand and inside temperatures of test homes clearly distinguished adequately sized storage heating systems that use only off-peak electricity from inadequately sized systems.

Utilization of Electric Energy. Fig. 1 shows the daily electrical energy demand for one home as a function of the outside temperature (on a degree-day basis). It may be seen that there is considerable variability in electric energy demand for heating. The line drawn through the data points is a best fit (least mean square-fitted line), and its slope is a measure of the heat loss factor, UA, of the house. The figure is a thermal fingerprint of the house and its electric heat usage. The pattern of residuals (deviations of points from the line) indicates the actual variability in electric heat demand that can occur for a given degree-day. The deviations from the line shown that other factors influence the electric heat demand. Each house exhibits its own, variable, pattern of energy demand that is related not only to its intrinsic heat loss but to other factors, making analysis difficult. We have begun statistically comparing ensembles of TES and control homes having similar heat loss values. A preliminary result is shown in Fig. 2. The procedure allows us roughly to compare the relative thermal performance of room unit TES and direct heating (baseboard) systems, (but not completely eliminating factors other than heat loss). Since both types of heating system operate by I^2R heat generation (100% efficient), approxiately the same amount of electrical energy should be required to meet a thermal demand. This is so at the crossover point but not elsewhere. Tentatively it may be said that TES homes use more electrical energy than control homes on warmer days and less on colder.

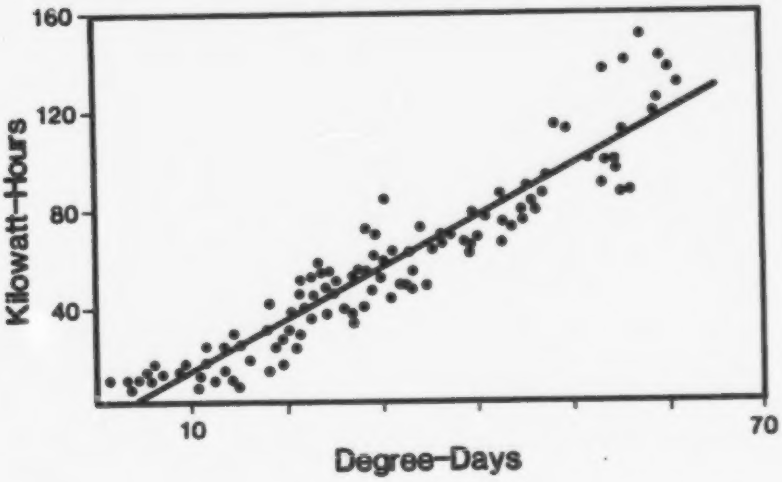

Fig. 1 Relation of Daily Electric Heat Demand and Degree-Day for House No. 2M in Maine

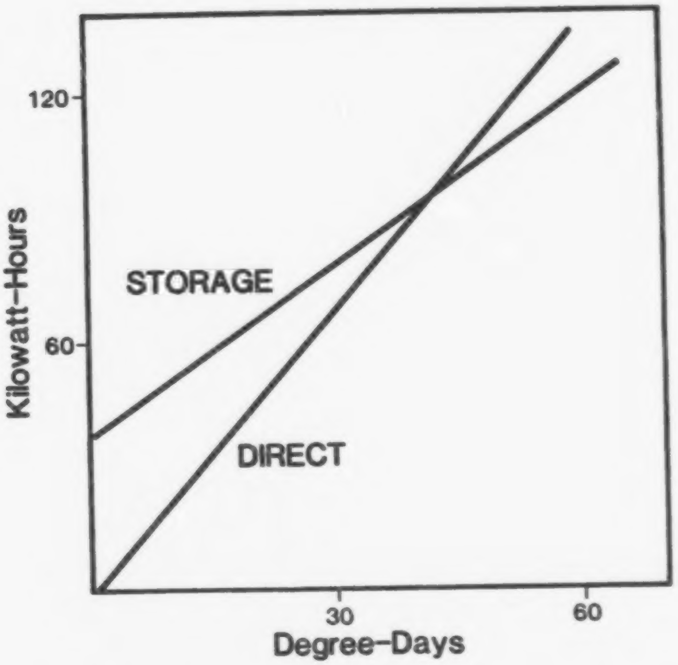

Fig. 2 Result of Statistical Analysis for Ensembles of TES and Control Homes in Vermont Having Similar Heat Loss

A similar observation has previously been reported for central storage heating systems. If the TES home overconsumption of energy on the milder days is due to the TES system per se, it might be associated with the minimum standby charge needed for an unexpected temperature drop. Uncertainty in the weather sets a fundamental limit to the performance of TES systems. We find that a combination of manual and automatic control results in better electric energy utilization, and more thermal comfort, than reliance on last night's weather.

Sizing. The sizing of storage systems involves additional considerations than in case of direct systems. Installation of units having both the proper connected load (kW) thermal capacity (kWh) is critical because of the high initial cost of the TES heating system (about 3 times that of baseboard). Undersizing, on the other hand, leads to shortfalls of heat late in the on-peak period, resulting in no heat or in using on-peak electricity. A building thermal performance simulation has been used to investigate sizing. Fig. 3 shows the stored charge as a function of time for one of the homes on the coldest day of the 1978/79 season. The connected load was 2.3 times the audited heat loss. It may be seen that there is a 20 percent carryover to the next day. The factor of 2.3 represents a conservative sizing level. An analysis is underway to specify the optimal sizing.

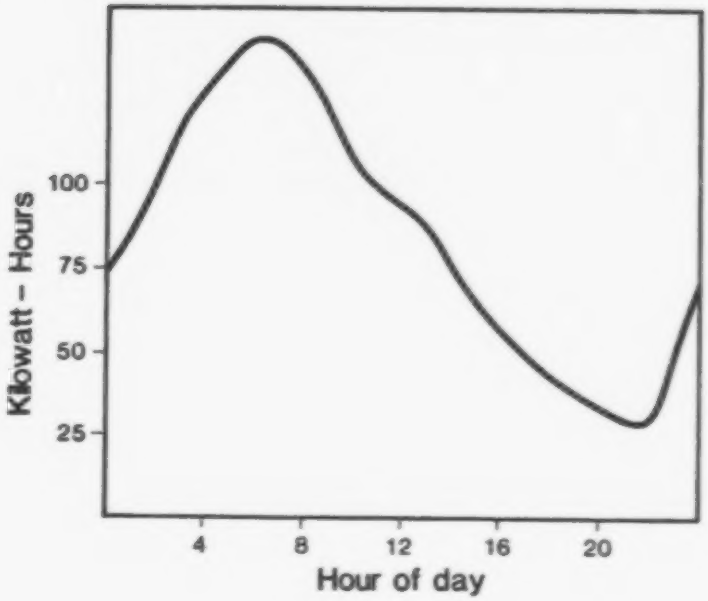

Fig. 3 Stored Charge on February 14, 1979 for TES Heating System in Maine with Connected Load 2.3 Times Calculated Heat Loss (Simulated)

3.2 ECONOMIC

User acceptance. In Vermont, on February 14, 1979, several homes had insufficient heat. During a recent site visit, a home-owner was asked whether this biased him against his system. He said (paraphrased) "I remember it well. It was bitter cold that day and we had to use blankets, but no, I feel that the low electrical bills more than made up for it. Those things don't happen frequently and we have to expect it."

Benefits and Costs. It has been previously determined that there would be net societal benefits if there were significant market penetration of TES in electric service areas that use oil and gas for peak power generation. The keys to market penetration are lower manufacturing costs and proper rates.

It has previously been anticipated that, at sufficient penetration, individual substations would require additions to capacity. In some heating districts in the service area of Central Vermont Public Service System (CVPS), saturation already exists, and additional TES units are not allowed in the subsystem (this can be controlled by not offering new load management contracts in those districts). If other factors did not change this would still allow the utility to offer TES in other parts of the system. Rates, however, may change.

Rates. A new storage heating contract offered by CVPS imposes a monthly equipment charge of 4.24¢/kW ($9.70 minimum) which will make it less attractive to potential buyers of TES heating systems than heretofor. The storage rate and the time-of-use (TOU) rate both offer lower electric bills than the standard rate, but there is now little difference in electric bills for direct heating using time-of-use rates and storage heating using the new storage rate. For a home with heat loss of 10kW, the estimated annual electric heat energy consumption is 15060 kWh/yr. For a direct heating system (12kW installed capacity) the total annual heating cost under the standard residential rate is $1287; under the time-of-use rate, using wood/coal as a backup to electric baseboard or a local time-of-use controller and electric ceiling heat, the cost can be a $700-850; and under the present storage rate, the annual heating cost would be $581. The TOU rate and the storage rate both offer a payback in about 3 years relative to the standard rate, but the present TES owner is not allowed to switch to a TOU rate to achieve additional heating cost savings; more importantly, prospective TES owners may choose to use a direct heating system with TOU rates, especially when one considers the cost of direct heating systems.

Equipment Cost & Economics. Installed TES systems cost at least three times as much as direct heating systems. An effort is underway to reduce the manufacturing cost by using domestic olivine bricks rather than foreign magnesite storage bricks. At the present time, however, ceramic TES systems are economically unattractive. The installation cost of a 20kW storage system for a house with a 10kW heat loss might be $3500 ± 300; and $1000 ± 100 for a 12kW direct heating electric ceiling system. The $2500 cost differential represents a lost opportunity to use this money at current interest rates. In New England, wood/coal burning is providing a backup for baseboard heaters. Electric ceiling heat is a recent contender for the electric heat market; it takes advantage of TOU rates and the characteristics of the system to consume only a minimum of electric energy during the peak period. For a 10kW house, the true amortized life cycle costs of baseboard with wood backup and electric ceiling heat can be less than that for TES ceramic heaters (Table 1).

Table 1 Representative Amortized Life Cycle Costs of Electric Heating Systems

	Storage[a]	Baseboard[b] with wood backup	Baseboard[c] (no backup)	Ceiling[d]
Installed Cost (± 10%)	$3500	$1000	$1000	$1000
Annual payment at 16%, 25 years	$ 562	$ 160	$ 160	$ 160
Percent on-peak	0	10	30	3
Annual electric heating cost	$ 581	$ 851	$1315	$ 691
Total annual cost (± 10%)	$1143	$1011	$1475	$ 851

[a] Ceramic storage heater, 20 kW connected load.

[b] 12 kW connected load; wood/coal backup, customer-managed.

[c] 12kW connected load; no backup.

[d] 12 kW connected load, time-of-use controller.

4 CONCLUSION

The technical viability of TES and acceptability to users have been established. Work in progress is concerned with possible technical shortcomings and economic difficulties which may slow TES market growth. Compared to direct heating devices, the utilization of electricity on warmer days of storage devices appears to be less efficient. The high life-cycle cost of TES systems relative to direct systems is a problem. In addition changes in utility rates may encourage the adoption of direct heating systems using time-of-use rates.

PROJECT SUMMARY

Project Title: Assessment of Cool Storage in Commercial Building Applications

Principal Investigator: Joseph G. Asbury

Organization:
Argonne National Laboratory
Energy and Environmental Systems Division
Argonne, IL 60439

Project Goals: The objectives of the study are: (i) determine the cost-effectiveness of cool storage as a load management technique, (ii) define the technical requirements of cost-effective storage devices, and (iii) specify R&D needs.

Project Status: The study is nearly completed; the final report is in preparation.

A case studies approach has been adopted to evaluate cool storage in commercial building applications. A number of basic storage concepts and relationships have been evaluated, including: load leveling vs. off-peak operation of the chiller, latent vs. sensible heat storage, new vs. retrofit applications, and the dependence of payback on width of building load profile.

Analysis of applications in two summer-peaking service areas indicates:

- Partial (load leveling) storage systems, because of their smaller compressor capacity requirements, offer faster payback than full storage systems.
- For the chiller water and ice storage cost values used in the analysis, chilled water storage offers a faster payback than ice systems in new applications. Ice systems may have the advantage in retrofit applications.
- Storage is more economical in buildings with short daily occupancy periods and narrow cooling loads than in buildings with longer occupancy periods.
- Paybacks of 2-4 years are possible in service areas where rate schedules are close to marginal cost values.

The following research and development needs were identified:

- Development of chillers and heat pumps to improve performance in the temperature regimes presented by cool storage systems.
- Identification of media and devices for cool storage at common utilization temperatures (38-44°F, 3-7°C) including consideration of sensible, latent, and reaction heat storage approaches.
- Evaluation of heat recovery potential in cool storage charging.
- Development of techniques for reduction of storage losses due both to mixing and to parasitic burdens.

Contract Number: AL-10-15/49961

Contract Period: October 1, 1979 through September 1, 1981

Funding Level: $150,000

Funding Source: U.S. Department of Energy, Office of Energy Systems Research, Technical and Economic Analysis Subprogram

ASSESSMENT OF COOL STORAGE IN COMMERCIAL BUILDING APPLICATIONS

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ABSTRACT

As part of its storage assessment program, Argonne National Laboratory is evaluating cool storage technologies for electric load leveling in commercial building applications. Analysis of conventional chilled water and ice storage systems indicate that paybacks of less than four years are available under the partial storage, or load leveling, mode of operation. Storage systems with sufficient capacity to eliminate on-peak chiller operations entail larger initial capital outlays and longer paybacks under existing commercial-class electric rate schedules. Improved performance and lower costs could be achieved through R&D to improve the match between the storage and the chiller systems and through development of improved latent heat systems.

I. INTRODUCTION

As part of its storage assessment program, Argonne is evaluating cool storage technologies for electric load leveling in commercial building applications. The basic objectives of the study are to define the technical requirements of cost-effective storage devices and to identify R&D needs.

Earlier work at Argonne has examined customer-owned storage in residential electric load leveling and solar heating applications.[1-6] In these studies, it was generally concluded that electric storage heating represented a cost-effective method of load management in service areas supplied by winter-peaking electric utilities, but that residential cool storage was only marginally cost-effective in service areas supplied by summer-peaking utilities. Analysis of storage in residential solar heating determined that storage was a necessary component of active solar systems if the systems were sized to meet a significant fraction of the daily heating load. However, on a total (utility plus customer) cost basis, the active solar systems generally were not cost-competitive with load managed electric systems.

The extension of the assessment of cool storage to cover the commercial building sector was prompted by the following observations:

- cool storage exhibits significant returns to scale, that is, the unit cost of storage decreases as the size of the storage system increases;
- the daily cooling cycles of commercial buildings are often of relatively short duration because of the short building occupancy period, thereby enabling a given amount of storage capacity (kWHs) to displace a proportionately greater demand (kWs) from the peak to the off-peak period;
- electric demand charges (or other marginal-cost-based electric rates) are more prevalent in the commercial sector than in the residential sector;
- commercial building applications usually offer greater opportunity for control of the operation of the cool storage equipment.

The balance of this report summarizes technical progress on the assessment of cool storage in commercial buildings. Section II discusses the performance and cost of cool storage systems, defines alternatives modes of operation of these systems, and describes the interface with conventional chiller systems. Section III presents an analysis of the payback on investment in cool storage and, finally, Section IV makes several R&D recommendations to improve the performance and economics of cool storage in commercial building applications.

II. COOL STORAGE TECHNOLOGY AND COSTS

Conventional cool storage systems are based on either ice-making (latent heat) or chilled water (sensible heat) storage. The basic principle of operation is to shift a substantial part of the electrical requirement for building space cooling from the utility's peak to its off-peak period. Depending upon changes in the temperature regimes faced by the evaporator and condenser coils of the chiller, this shifting of the electrical load will affect the number of kilowatt-hours consumed by the customer; it may, in fact, lead to increased consumption. The load shifting, however, will reduce the demand, or capacity, component of cost and will enable the utility to supply more of the customer's electrical requirement with lower-cost off-peak fuel. An added conservation benefit accrues because the off-peak utility generating plant is generally more energy-efficient than the plant used to supply on-peak electricity.

Whether ice or chilled water storage is used, a key consideration, affecting the sizing and operation of the storage and chiller components, is the mode of operation selected.

Full vs. Partial Storage

Under the full storage, or off-peak, mode of operation, the compressor and storage capacities are selected to enable the system to supply most of the building cooling needs during the peak period from storage. In this mode of operation, the chiller is switched off during the peak period so that the only cooling-associated loads during the peak period are those due to the operation of water circulation pumps and blowers in the building water distribution and air handler systems. Storage capacity must be adequate to meet the time-integrated building load during the peak period plus the thermal losses from storage on the design day. The full-storage concept minimizes the contribution of the building cooling load to the utility's coincident peak load.

Under the partial storage, or load-leveling, concept the storage and chiller capacities are set by the criterion that the design day load be met by continuous operation of the chiller at rated output. This mode of operation minimizes the chiller capacity requirement. The load profile and the capacity trade-offs for conventional, full-storage, and partial-storage systems are illustrated in a simple way in Fig. 1.

Latent vs. Sensible Heat Storage

Water-based cool storage systems make use of either the sensible heat content (1 Btu/°F/lb) or the latent heat of fusion (144 Btu/°F/lb) of water.

An important consideration in the design of sensible storage is the inlet temperature requirements of the water distribution system. For reasons of humidity control and adequate heat exchange at the air handler, the water temperature at the inlet to the distribution system is generally held to 48°F or less, corresponding to a return temperature on the design day in the range 55-59°F. Thus, because the temperature swing available for sensible heat storage is constrained to lie between the freezing point of water and 48°F, the maximum ΔT for design purposes is approximately 15°F.

If the sensible heat storage system incorporates a stratified chilled water storage tank, the water supplied to the distribution system from the bottom of the storage tank can be held to 40°F, the temperature at which the specific gravity of water is greatest. In principle, under conditions of perfect stratification, this temperature can be maintained over the entire diurnal cycle. If the return temperature from the air handler systems rises to 58°F on the design day, the ΔT available for storage is 18°F. In practice, the finite thickness of the stratification layer in the storage tank will cause the temperature at the inlet to the distribution system to rise above 40°F on the design day if the storage tank is sized

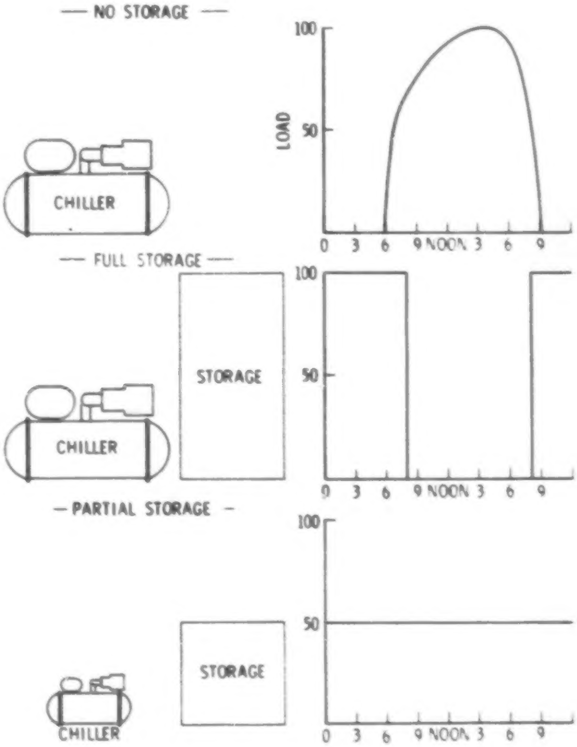

Fig. 1. Operating Modes for Cool Storage Systems

under the assumption of perfect stratification. Experience with the operation of stratified cool storage tanks indicates that the degradation caused by such effects is about 20% of original design capacity. Thus, for design purposes, a ΔT equal to 15°F again can be assumed.

The unit cost of chilled water storage varies widely, depending on such factors as storage tank material, storage size and location, and whether the storage is for old or new construction. Figure 2 presents cool storage costs as a function of storage size as determined by recent engineering design studies and actual experience in constructing storage tanks.[7] The storage costs shown in the figure refer to bare tank costs, in this case the cost of cast-in-place concrete tanks. Such tanks are generally regarded as the lowest cost storage for capacities in excess of 40,000 gallons, or 400 ton-hours.

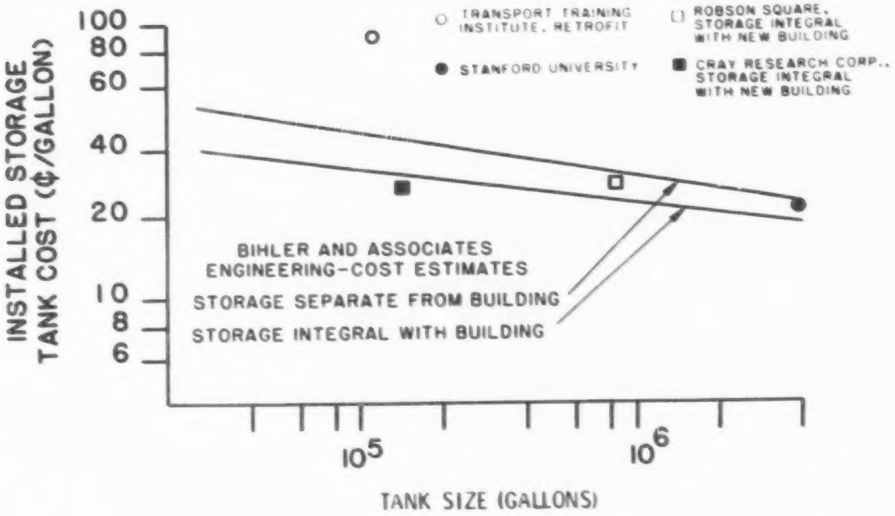

Fig. 2. Cost of Cast-in-Place Concrete Tanks as a Function of Storage Tank Size

To obtain an estimate of the total cost of chilled water storage systems, the cost of piping, controls, and instrumentation must be added to the tank costs. Two recent cost studies, one based on an engineering cost analysis,[8] the other on actual experience at Robson Square,[9] indicate that the cost of the basic storage tank should be increased by approximately 50% to account for balance-of-system costs.

The main advantage of ice over chilled water storage is the smaller storage volume required. Were it possible to cycle the entire storage volume between solid and liquid phases, an ice storage system would offer an order-of-magnitude volume reduction relative to a chilled water system with ΔT = 15°F. In practice, because of the need to maintain part of the storage medium in the liquid phase (for circulation and heat transfer) and because of the presence of evaporator coils in the ice-building systems, the volume savings are limited to about a factor of six.

Ice systems fall into two general categories: static (ice-building) systems and dynamic (ice shucking or slurry) systems. In the static systems, ice is formed on evaporator coils incorporated into the storage tank itself. The static systems include ice-thickness control and either internal baffling or water agitation for efficient heat transfer from ice surfaces during the melting cycle.

Dynamic ice storage systems manufacture ice in crushed or chunk form and deliver it for storage in large bins. The storage tanks for dynamic systems are similar in design and operation to those used in the chilled water systems.

An inherent disadvantage of the ice systems, relative to the chilled water systems, is the lower suction temperature required of the chiller, typically 10°F for ice building vs. 30°F for chilled water systems, causing significant reductions in chiller capacity and energy efficiency.

The cost of ice storage, including shipping costs and contractor installation, overhead, and profit, is approximately $0.60 per pound of ice capacity for packaged systems of 45,000 pound capacity.

Unit costs rise with smaller size, to approximately $1.65/lb for packaged systems of 4,000 lb capacity. Figure 3, based on vendor price lists, shows the dependence of unit cost on storage capacity.

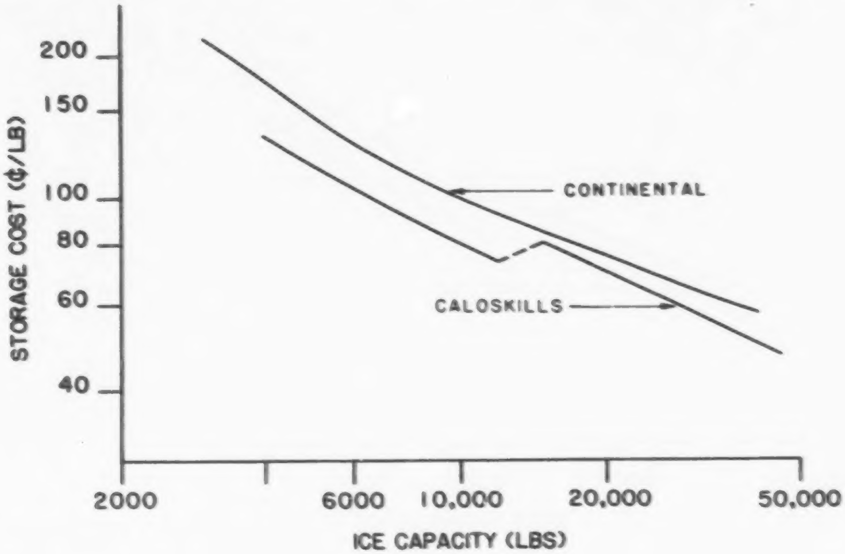

Fig. 3. Cost of Ice Storage Equipment

Chiller Systems

The storage systems described above must be matched with an appropriate chiller system and integrated into a complete building air conditioning system.

Three types of compressive chillers -- reciprocating, centrifugal, and screw -- are currently available for commercial building use. In recent years the range of applicability of screw compressors has been extended to approximately 800 tons. Although the application of screw compressors to space conditioning is a relatively new development, occurring within the last seven or eight years, screw compressors have been used in the refrigeration field for about fifteen years.

Figure 4 shows installed system costs for systems incorporating packaged compressive chillers.[10] The system costs include the costs of the packaged chiller, the cooling tower, and the condenser water pumps, plus installation costs, including contractor overhead and profit. As indicated in the figure, reciprocating systems represent the lowest cost alternative below 120 tons capacity, while screw-type compressors are less expensive above 120 tons.

Compressor performance depends on the saturated suction temperature (SST) and saturated discharge temperature (SDT). For a constant SDT, compressor capacity and coefficient of performance (COP) decline with decreasing SST. On the other hand, for constant SST, both capacity and COP increase with decreasing SDT.

Because the operation of a storage system involves a lower SST than does the operation of conventional cooling system (SST equals 30°F for chilled water and 10°F for ice storage vs. 34°F for a conventional system), chiller performance is correspondingly diminished. This loss in performance may be partly or completely made up, however, by the lowest SDT available to cool storage systems. The lower SDT occurs because of proportionately longer operation of cool storage systems during the nighttime hours when outdoor temperatures are lower. Table 1 shows compressor performance for different SDT and SST values.

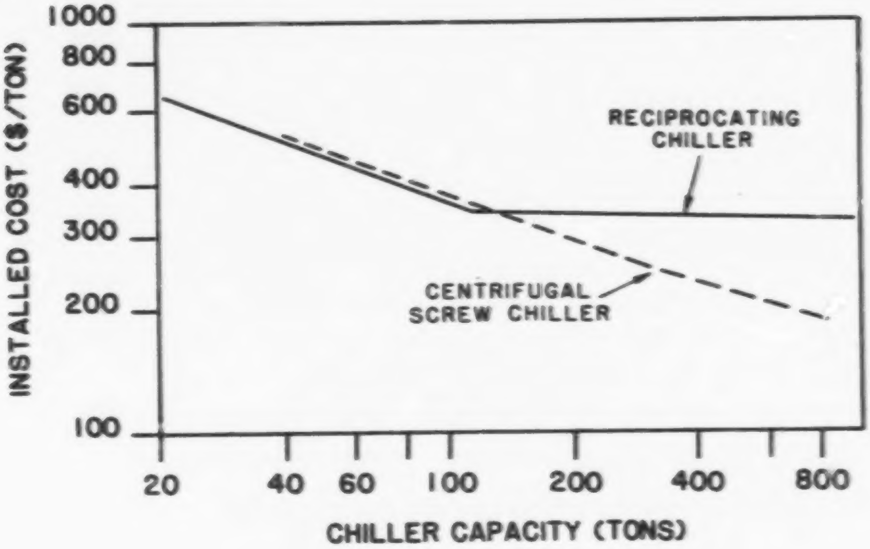

Fig. 4. Costs of Installed Chiller Systems

Table 1. Changes in Compressor Performance with Changes in Saturated Suction Temperature and Saturated Discharge Temperature

	Reciprocating Compressor				Screw Compressor			
System	Saturated Suction Temperature (°F)	Saturated Discharge Temperature (°F)	Relative Capacity	Relative COP	Saturated Suction Temperature (°F)	Saturated Discharge Temperature (°F)	Relative Capacity	Relative COP
Conventional	34	105	1.00	1.00	34	105	1.00	1.00
Chilled Water Storage	30	105	.98	1.00	30	105	.94	.94
	30	95	1.04	1.15	30	95	1.00	1.17
	30	85	1.14	1.40	30	85	1.07	1.45
Ice-Building Storage	10	105	.57	.70	10	105	.61	.65
	10	95	.62	.80	10	95	.67	.76
	10	85	.69	.94	10	85	.70	.85

III. EXAMPLE APPLICATIONS

The overall costs of installing and operating cool storage systems were compared with the costs of conventional systems in representative commercial buildings in two service areas. One service area is located in the Mid-Atlantic region; the other in the Midwest. Both are supplied by summer-peaking utilities that have adopted peak load rates for large commercial-class customers. Eight buildings (four in each service area) were analyzed; results for one of the buildings in the Mid-Atlantic service area are presented here.

Load Analysis

Actual building electric loads, measured on a 15-minute interval basis by the local utility, were used to characterize the building cooling loads. To size both the conventional and the cool storage HVAC systems, it was necessary to estimate thermal cooling loads under design-day conditions. A two-step procedure was used to separate the measured building electrical loads into weather-sensitive (thermal) and weather-neutral (non-thermal) components. First, a weather-neutral load profile was estimated for each weekday by identifying that Spring day with minimum integrated building load (holidays excluded). Next, the Summer day with maximum demand was identified. The design-day hourly cooling load was then estimated as the difference between the profiles on the peak and weather-neutral days.

Engineering Design

The cooling system was assumed to consist of a central-electric chiller, cooling tower, auxiliaries, and a water distribution system having an inlet water temperature of 44°F. The electric chiller, a screw compressor, was assumed to have a COP of 3.5. Under these assumptions, one ton-hour of building thermal load corresponded to an electrical requirement of one kilowatt-hour.

The following sizing criteria were used:

Conventional System: The conventional systems were sized to meet the annual peak hourly thermal load.

Partial Storage System: The partial storage systems were sized to meet the time-integrated thermal load on the design day under continuous operation of the compressor. Although the compressor operates continuously at full capacity on the design-day, changes in compressor performance with day-night variations in suction temperature have the effect of reducing the nighttime electrical load relative to the daytime load.

Full Storage System: The full-storage systems were sized to minimize building peak electrical load during the peak demand period by shifting the cooling load into the off-peak, nighttime period.

The sizing of the ice systems included an adjustment to account for the non-linear buildup of ice on the evaporator coils over time. A set of relationships develoed by Caloskills was used for this purpose.[11]

System Costs

Component sizes and costs for the different cooling system alternatives under the partial and full storage modes of operation are shown for a representative building in Table 2. The capital costs of the cooling system incorporating partial storage are about 70% higher than for the conventional

Table 2. System Sizes and Costs

		Partial Storage		Full Storage	
Equipment Description	Conventional	Ice-Building	Chilled Water	Ice-Building	Chilled Water
Component Sizes					
Compressor (Tons)	2-805	2-395	2-330	2-810	2-535
Storage Tank	--	5,600 ton-hr	792,000 gal	12,760 ton-hr	1,304,000 gal
Storage Volume	--	20'x25'x25'	20'x70'x75'	20'x35'x40'	20'x90'x95'
Compressor Demand (kW)*					
Daytime	1605	790	655	0	0
Nighttime	--	695	560	1430	905
Component Costs (1980 $$10^3$)					
Chiller System					
Chiller	211.9	143.7	129.6	213.2	171.4
Cooling Tower	55.2	28.7	23.7	55.7	36.6
Condenser Pump	8.3	4.3	3.8	7.4	5.5
Installation	26.6	12.9	11.4	26.9	17.7
Storage System	--	320.9	309.5	556.1	467.4
Total	302.0	510.5	478.0	859.3	698.4

*Represents electrical load under design-day operating conditions.

cooling system, the added costs of storage being partly offset by the chiller capacity savings. Both the ice-building and the retrofit chilled water systems cost substantially more than the conventional system.

As indicated in the table, the capital costs of full storage system are substantially greater than the capital cost of the partial storage system.

Customer Payback Analysis

Because the storage systems entail a higher initial cost than the conventional cooling system, the cost-effectiveness of storage depends upon savings available under the applicable electric utility rate schedule. Customer bill savings were computed under the rate schedule currently in force in the Mid-Atlantic service areas. The rate schedule is a time-of-use schedule incorporating energy and demand changes and three daily and two seasonal demand periods.

Monthly energy and demand changes were computed and summed over an annual cycle to determine annual bills for the different systems. Table 3 presents annual energy consumption and peak demands and the associated bill values for each of the cooling systems. Simple paybacks on investment in the alternative storage system were calculated based on the system bill savings in Table 3 and the system costs given in Table 2. The results of the payback analysis are presented in Table 4.

Table 3. Annual Cooling Loads and Bill Values

	Cooling Load		Annual Bill		
System	Peak* (kW)	Energy (MWh)	Demand ($10^3$$)	Energy ($10^3$$)	Total ($10^3$$)
Conventional	1605	1859	116.2	54.8	171.0
Chilled Water					
Partial Storage	655	1715	47.7	49.2	96.9
Full Storage	0	1584	0	43.6	43.6
Ice-Building					
Partial Storage	790	2095	57.5	60.1	117.6
Full Storage	0	2448	0	67.5	67.5

*Refers to contribution of cooling load to building peak demand during peak demand period.

Table 4. Payback on Investment in Cool Storage

		Incremental Investment ($10^3$$)		Payback (Years)	
System	Bill Savings ($10^3$$)	New	Retrofit	New	Retrofit
Chilled Water					
Partial Storage	74.1	176.0	330.7*	2.4	4.5
Full Storage	127.4	396.6	630.3*	3.1	4.9
Ice-Building					
Partial Storage	53.4	208.5	208.5	3.9	3.9
Full Storage	103.5	557.3	557.3	5.4	5.4

*Based on a retrofit cost for the storage component of a chilled water system equal to 1.5 times the cost for a new system.

The results for this example application, combined with results for the other buildings, lead to the following conclusions:

- Partial storage systems, because of their smaller compressor capacity requirements, involve substantially lower capital outlays by building owners than do full storage systems; partial storage also offers faster payback than full storage.
- For the storage cost values used in this analysis, chilled water storage offers a faster payback than ice systems in new applications. Ice systems may have the advantage in retrofit applications. (See Reference 12.)
- Storage is more economical in buildings with short daily occupancy periods and narrow cooling loads than in buildings with longer occupancy period.[12]

IV. RESEARCH AND DEVELOPMENT NEEDS

The analysis of cool storage described above is based on adoption of commercially available hardware components. Refinement of these devices for optimal application in storage systems will improve their performance and reduce costs. Manufacturers of tanks, ice builders, and similar devices have begun to address improvements to their products and marketing approaches. Further technology development requires public-sector participation due to the inherent levels of risk and delays in return on RD&D efforts. Several R&D needs have been identified for DOE consideration, and their requirements and potential benefits are being addressed. These include:

- Development of chillers and heat pumps to improve performance in the temperature regimes presented by cool storage systems;
- Identification of media and devices for cool storage at common utilization temperatures (38-44°F, 3-7°C) including consideration of sensible, latent, and reaction heat storage approaches;
- Evaluation of heat recovery potential in cool storage charging;
- Examination of economies of scale in even larger applications, for example, in central and district heating and cooling systems; and
- Development of techniques for reduction of storage losses due both to mixing and to parasitic burdens.

A fuller discussion of these issues is provided in a forthcoming report.[12]

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PROJECT SUMMARY

Project Title: Pelletization and Encapsulation of Phase Change Materials

Principal Investigator: Johnson Chen

Organization:
Pennwalt Corporation
Central Research & Development
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Project Goals: Develop reliable and cost effective capsules of phase change materials (PCMs) for use in: (i) active heat exchange packed-bed assemblies of simple design that will provide heat exchange efficiency and storage capacity superior to those of conventional heat storage systems; and (ii) passive heat storage systems consisting of building products incorporating thermal energy storage (TES) materials.

Project Status:

- The project is in the final phase of investigation.
- Seven PCM candidates have been successfully formed into pill-size tablets and coated with various organic coating materials.
- Accelerated thermal cycling tests show that four of the seven PCM candidates have good physico-chemical stabilities in various aqueous heat exchange fluids.
- The preferred PCM capsule/heat exchange fluid combinations are being tested for long term stability and heat transfer efficiency in a packed-bed thermal cycling assembly.
- Tablets of Glauber's salt eutectic mixture coated with Geon 660X1 (a vinylidene chloride-acrylic copolymer) and asphalt are showing good stability in the laboratory air environment.
- An economic analysis has shown that the cost of the PCM capsules will be well within the predicted competitive cost range.

Contract Number: 31-109-38-5900

Contract Period: 1 October 1980 to 31 October 1981

Funding Level: $90,158

Funding Source: U. S. Department of Energy-Argonne National Laboratory

PELLETIZATION AND ROLL ENCAPSULATION OF PHASE CHANGE MATERIALS

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ABSTRACT

Based on the criteria of high latent heats of fusion, low cost, and ease of pelletization, seven phase change materials (PCMs) with melting points in the ranges suitable for absorption cooling, active heating, and passive space conditioning applications have been pressed into pellets about 12 mm in diameter and then encapsulated with organic coating materials by a roll coating process. Capsules of four of the seven PCM candidates have shown retention of integrity in various aqueous heat exchange fluids in accelerated thermal cycling tests ranging between 1500 to 2900 heating and cooling cycles. Capsules of PCMs melting near room temperature have also shown good stability in laboratory air environment. The objective of this effort is to develop reliable and cost effective PCMs for use in: (i) active heat exchange packed-bed assemblies of simple design that are capable of providing heat exchange efficiency and storage capacity superior to those of conventional heat storage systems, and (ii) passive heat storage systems consisting of building products incorporating thermal energy storage (TES) materials. The feasibility of this approach is supported by a favorable cost analysis.

BACKGROUND

Phase change materials (PCMs) for thermal energy storage (TES) applications offer advantages over materials whose thermal storage capacity is based exclusively on sensible heat. These advantages consist of: (i) higher energy density, (ii) smaller Δt, and (iii) higher heat collection efficiency. Problems with the use of PCMs may consist of slow heat transfer rate and possible materials degradation (phase separation). Efficient and cost effective application of PCMs in heat storage systems depends on the solution of these problems. Approaches to their solution include development of suitable packaging materials and configurations for the PCMs and/or modifications in heat exchange systems design.

A number of innovative ideas have been developed and reported.(1-6) Each approach offers partial solutions to the heat storage problem. A solution that combines the advantages of flexibility in materials selection, full utilization of latent heat, high heat efficiency, and long term reliability of the heat storage system is yet to be discovered.

Pennwalt Corporation, under contract with Argonne National Laboratory/U. S. Department of Energy, is investigating a packaging process that is applicable to a large variety of PCMs and should alleviate the problem of phase separation. A successful development of this approach may lead to active TES systems with high heat storage capacity and high heat transfer rates. Moreover, the PCM capsules with melting points suitable for passive storage applications can also be incorporated into building components to increase the thermal mass of a building without detrimental PCM interference with the construction materials. The process consists of pressing the PCMs into tablets by means of a pelletizing machine (Figure 1) followed by encapsulation of the tablets with suitable coating materials in a rotating drum (Figure 2). This study was devoted to PCMs suitable for space heating and cooling applications (melting range 7-120°C).

SELECTION AND PELLETIZATION OF PCMs

The candidate PCMs listed in Table 1 meet the following criteria: (i) high latent heat, (ii) ease of pelletization, (iii) low cost, and (iv) appropriate phase change temperatures for designated applications, i.e., absorption air conditioning (85°C and above), active heating (35-60°C), passive space conditioning and heat pump augmentation (20-30°C), and cold storage (7-10°C). The candidate materials for cold storage were found to be unsatisfactory for pelletization, and therefore none were selected for further study.

The pelletizing machine used in this investigation requires that the PCM powders to be pelletized are free flowing. The PCMs have therefore first been reduced by appropriate treatment to the size and properties required by the machine. Crushing and grading techniques have been used for inorganic salt hydrates. Minute amounts (0.3-5%) of additives such as fumed silica and lithium stearate have been used to improve release from the mold. The wax used in this investigation (P116, m. p. 46°C) does not form firm tablets; the problem has been solved by adding calcium stearate (5%) which improves the compacting and mold release properties. The modified wax has then been reduced to the suitable particle size range by melting and dispersing in water. With the technique described above, all seven candidate PCMs have been pelletized to cylindrical tablets 8 mm to 12 mm in diameter and 3 mm to 6 mm in thickness with both convex and concave surfaces.

ROLL ENCAPSULATION

The purpose of encapsulation is to provide a continuous, non-porous wall around the PCM core. This is accomplished by tumbling the PCM tablets in a rotating drum (Figure 2) with intermittent addition of coating materials. An air stream is used to assist drying of solvents. In order to minimize cost and pollution, water-borne latex formulations have been selected as the principal coating materials. In some cases, a thin layer of solvent-borne coating was applied as primer.

With proper precautions, capsules of all seven PCMs were made with 10-25% wall content. Efforts are being made to reduce the wall content and thus increase the heat capacity of the PCM capsules. The preferred combinations of PCM tablets and coating materials are summarized in Table 2.

In order to further reduce the cost of coating materials for capsules designed for use in building products, blends of latex and asphalt emulsions are also under investigation.

HEAT EXCHANGE FLUIDS AND SMALL SCALE CYCLING TESTS

The encapsulated PCM tablets must be able to maintain mechanical and chemical integrity over long periods of time under thermal cycling conditions. This requires wall materials tough enough to withstand the thermal expansion and contraction of the PCM core during thermal cycling and provide an effective, long-lasting barrier between the PCM and heat exchange fluid. As a consequence, the nature of the heat exchange fluid is also a critical parameter. An ideal heat exchange fluid for use with PCM capsules in active storage systems should be: (i) high in specific heat, (ii) inert to the capsule wall material, (iii) low in toxicity, (iv) low in viscosity, and (v) inexpensive. Water meets all these requirements, and therefore, all capsules of the seven PCMs studied were subjected to thermal cycling in water. Wax capsules sustained over 2900 accelerated heating and cooling cycles without noticeable adverse effects other than swelled polymer wall. With capsules of inorganic salt hydrates, water permeated the organic capsule walls and destroyed the phase changing properties after several hundred thermal cycles. In order to eliminate wall swelling in wax capsules and establish water vapor pressure balance on both sides of walls of inorganic PCM capsules, aqueous solutions of ethylene glycol and $CaCl_2$ were studied in place of pure water. Encapsulated wax showed good retention of configurations after 2900 cycles (Figure 3) in ethylene glycol solutions of various concentrations. Capsules of $Na_2S_2O_3 \cdot 5H_2O$ and Glauber's salt eutectic mixture also showed good thermal cycling results in ethylene glycol solutions. Promising results were also obtained with concentrated aqueous $CaCl_2$ solutions (30-35%) in the case of Na HPO 12H O and Glauber's salt eutectic mixture. $MgCl_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ failed after several hundred thermal cycles in all the aqueous solutions tested. Table 3 summarizes the results of thermal cycling of encapsulated PCMs in various aqueous heat exchange fluids.

PACKED BED CYCLING TESTS

The successful combinations of PCMs and heat exchange fluids were then subjected to long term thermal cycling evaluation in a packed-bed assembly (Figures 4, 5, 6). Hot and cold heat exchange fluids are circulated alternately through the bed packed with PCM capsules. From this test, heat storage capacity, heat transfer efficiency, and long term stability are evaluated. At the time of this writing eight hundred grams of wax capsules have been under thermal cycling for more than 250 cycles without significant problems using water as heat exchange fluid. Good temperature distribution across the bed was observed both in the heating and cooling modes.

AIR EXPOSURE TESTS

Because building materials are subjected to air environment aging, the PCM capsules intended for use in building components should have good stability when exposed to air. Capsules of Glauber's salt eutectic mixture have therefore been exposed to laboratory air environment for extended periods of time. Pellets with wall contents of 15% or more are showing good stability (Table 4). For example, the capsules with 15% of Geon 660X1 (a vinylidene chloride-acrylic copolymer) have suffered only 1.4% weight loss after 95 days of exposure comparing to 6.7% weight loss for those containing only 10% of the same wall materials after 69 days.

APPLICATIONS OF ENCAPSULATED PCMs

Encapsulated PCMs, being self-contained and possessing high surface area, enable construction of heat storage assemblies of simple design, high storage capacity, and high heat transfer efficiency. They will be particularly effective in solar, waste heat recovery, and other low-grade heat storage applications, either active or passive. Of special interest is incorporation of encapsulated PCMs in structural building components such as concrete and plaster walls.(7)

ECONOMIC ANALYSIS

An estimate was made of the cost of the pelletization and encapsulation process using commercial industrial-size tabletting and roll coating equipment similar in design to the laboratory-size equipment being used for this project. For production quantities of 0.5-50 MM lb/year, the manufacturing price, inclusive of the cost of coating materials, is estimated to be about 20¢/lb. When the cost of the PCM material is added (5-20¢/lb) the resulting selling price for the capsules appears to be within the predicted competitive cost range ($\leq$ 40¢/lb),(5) especially for capsules of inorganic salt hydrates.

CONCLUSIONS

All seven candidate PCMs have been pelletized into pill-size tablets and successfully coated with organic polymer coating formulations. Accelerated thermal cycling tests of these capsules in various aqueous heat transfer fluids have thus far shown that four of the seven candidates maintain good physico-chemical integrity for over 1500 and up to 2900 heating and cooling cycles. This simulates 10-25 years of real world application. Capsules of these four PCMs are good candidates for scale-up studies in packed bed heat storage assemblies for active storage applications.

The good air exposure stability of the capsules of Glauber's salt eutectic mixture suggest that these capsules are good candidates for inclusion into building components for passive storage applications.

A favorable cost analysis further supports the approach of using encapsulated PCMs for heat storage applications.

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TABLE 1

MATERIALS UNDER INVESTIGATION

MATERIAL	COST (¢/LB)	ΔH(BTU/LB)	PHASE CHANGE TEMPERATURE (°F)	APPLICATION (TEMPERATURE RANGE)
$MgCl_2 \cdot 6H_2O$	12	72	242	Absorption cooling (185°F and above)
$Mg(NO_3)_2 \cdot 6H_2O$	32	68	185	
$Na_2S_2O_3 \cdot 5H_2O$	12	86	120	Active Heating (95-140°F)
Wax P116	20	63	116	
$Na_2HPO_4 \cdot 12H_2O$	20	114	97	
$CaCl_2 \cdot 6H_2O$	4	81	84	Passive Space Conditioning and Heat Pumps (68-86°F)
Glauber's Salt Eutectic Mixture	5-10	90	73	

TABLE 2

PCMs and Preferred Encapsulating Materials

PCMs	Coating Materials[a]
$MgCl_2 \cdot 6H_2O$	Acryloid B99; Good-Rite 2570X1; Geon 660X1; Hycar 1572
$MgNO_3 \cdot 6H_2O$	Geon 660X1; Good-Rite 2570X1; Acryloid B99; Hycar 1572
$Na_2S_2O_3 \cdot 5H_2O$	Geon 652; Geon 660X1; Good-Rite 25701X1
Wax (P116)	Hycar 1572; Good-Rite 2570X1
$Na_2HPO_4 \cdot 12H_2O$	Geon 660X1; Good-Rite 2570X1;Acryloid B99
$CaCl_2 \cdot 6H_2O$	Acryloid B99; Good-Rite 2570X1; Geon 660X1; Hycar 1572
Glauber's Salt Eutectic Mixture	Hycar 1562X159; Hycar 1800X73; Good-Rite 2570X1; Geon 660X1 and its asphalt blends

[a] Acryloid B99 is an acrylic polymer solution made by Rohm & Haas. Geon, Hycar and Good-Rite are trademarks of Goodrich Chemical Company. Geon 652 is a vinylidene chloride-vinyl chloride copolymer. Geon 660X1 is a vinylidene chloride-acrylic copolymer. Hycar 1561, 1562X159, 1800X73 are nitrile latexes. Good-Rite 2570X1 is a styrene-butadiene copolymer. As later shown, these coating materials are frequently used in multilayer combinations.

TABLE 3

THERMAL CYCLING TESTS OF ENCAPSULATED PCMs IN VARIOUS HEAT EXCHANGE FLUIDS

PCMs	Coating Materials	Heat Exchange Fluids													No. of Cycles Completed
		Water/Ethylene Glycol								$CaCl_2$ Solution (Wt.% of $CaCl_2$)					
		100/0	50/50	25/75	20/80	15/85	10/90	5/95	0/100	10	20	30	35	40	
$MgCl_2 \cdot 6H_2O$	Layered combination of Good-Rite 2570X1· Geon 660X1 and Hycar 1572										C	C	B	C	350
$Mg(NO_3)_2 \cdot 6H_2O$	Layered combination of Good-Rite 2570X1, and Geon 660X1												C	C	250
$Na_2S_2O_3 \cdot 5H_2O$	Same as above											B	B	C	650
					B										1700
	Geon 660X1		A	A											1500
Wax	Good-Rite 2570X1	B	A	A											2900
	Hycar 1572	A	A	A											2800
$Na_2HPO_4 \cdot 12H_2O$	Layered combination of Good-Rite 2570X1, and Geon 660X1						B								1700
											A	A	A		1900
$CaCl_2 \cdot 6H_2O$	Layered combination of Good-Rite 2570X1, Geon 660X1 and Hycar 1572											C		C	650
Glauber's Salt Eutectic Mixture	Geon 660X1		A	A											1700
													A		1900
	Blend Asphalt/Geon 660X1 (25/75)								A						650

A - Integrity Retained B - PCM Capsules Gain Weight C - Broken Wall D - Partial Retention of Integrity

TABLE 4

EXPOSURE OF PCM CAPSULES TO LABORATORY AIR ENVIRONMENT

Wall Inner Layer % (Asphalt/Geon 660X1/Hycar 1572)	Wall Outer Layer % (Geon 660X1)	Total Wall Content (%)*	Days Exposed	Weight Loss (%)
15 (50/50/0)	10	25	20	1.2
			39	1.6
10 (30/70/0)	10	20	20	.51
			63	1.0
15 (50/25/25)	10	25	10	.17
			33	1.0
0	15	15	26	.29
			32	.86
			39	.86
			47	1.1
			53	1.1
			95	1.4
0	10	10	6	.96
			12	2.5
			17	3.5
			27	4.2
			33	3.4
			69	6.7

*Percent of total weight of encapsulated tablets.

Figure 1. Tabletting Machine
(Pennwalt Stokes Model 900-511-6)

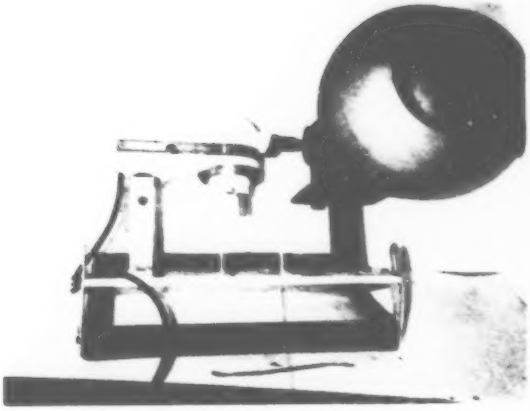
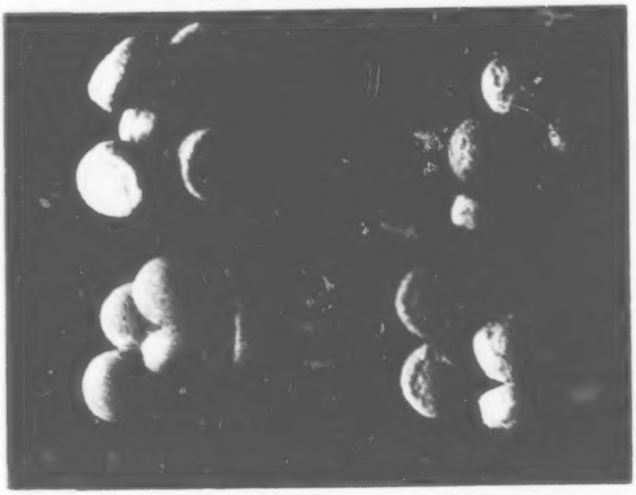


Figure 2. Roll Coater

After 2900 cycles in
50% ethylene glycol

After 2900 cycles in
75% ethylene glycol



Before cycling

After 2900 cycles in
ethylene glycol

Figure 3. Wax Capsules Before and After Thermal Cycling

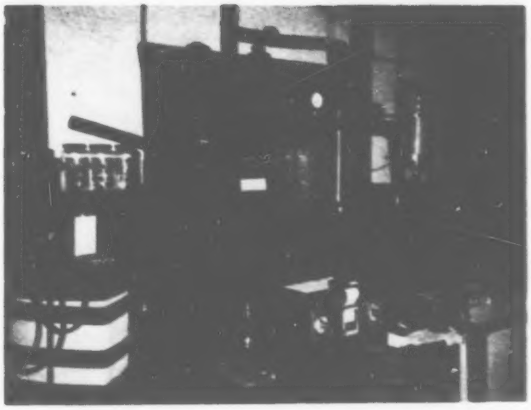


Figure 4. Packed Bed Cycling Machine

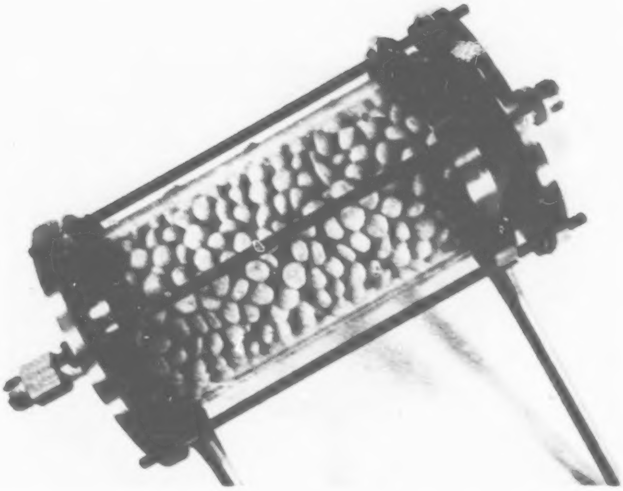
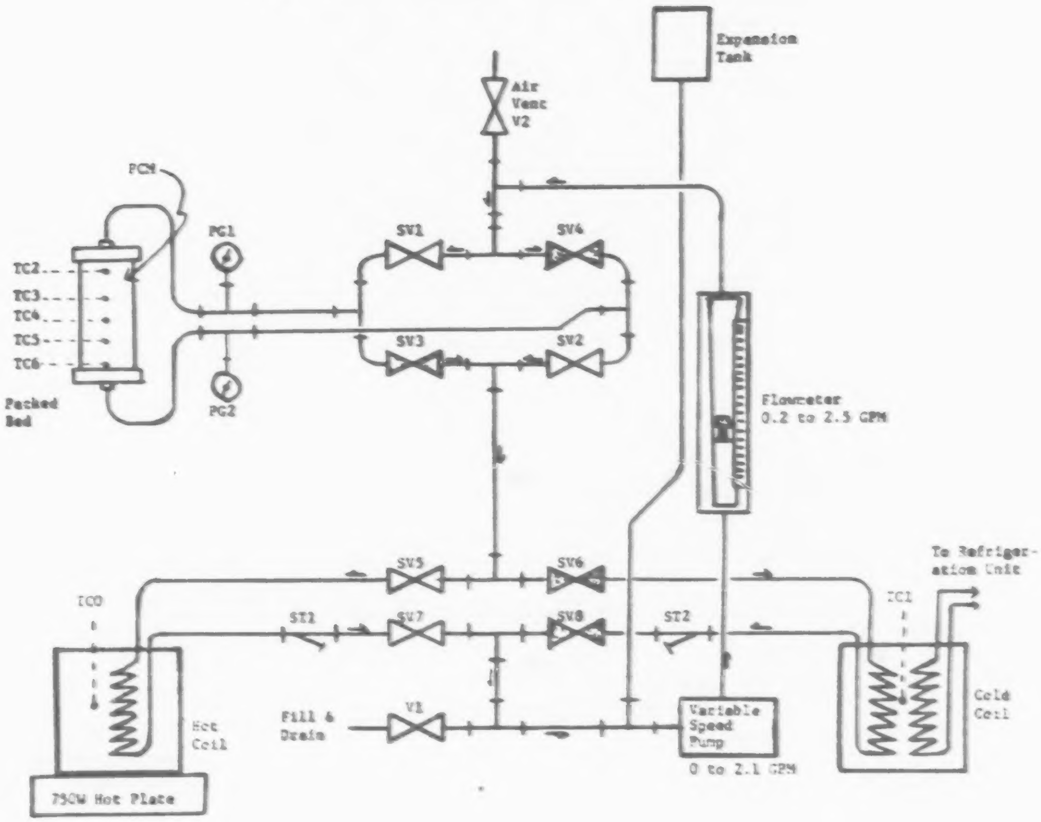


Figure 5. Packed Bed of Wax Capsules

Figure 6. PACKED BED THERMAL CYCLING DEVICE


Expansion Tank
Air Vent V2
PCM
PG1
SV1
SV4
TC2
TC3
TC4
TC5
TC6
SV3
SV2
Packed Bed
PG2
Flowmeter 0.2 to 2.5 GPM
To Refriger-ation Unit
SV5
SV6
TC0
ST1
SV7
SV8
ST2
TC1
Fill & Drain
V1
Variable Speed Pump
0 to 2.1 GPM
Hot Coil
Cold Coil
750W Hot Plate

PROJECT SUMMARY

Project Title:	Effect of Additives on Performance of Hydrated Salt TES Systems
Principal Investigator:	Calvin D. MacCracken
Organization:	Calmac Manufacturing Corporation P.O. Box 710 Englewood, N. J. 07631
Project Goals:	Test, evaluate, develop and report on the application of additives to various phase change materials for thermal energy storage originated by others which claim to affect stratification and subcooling
Project Status:	The project is half done. The British CALOR hydrogel method with sodium sulfate is in the early stages of evaluation due to time required to obtain certain information and chemicals from the U.K. Mixes with slight variations in formulation and procedure are being made to learn necessary parameters. Continuous automatic cycling tests of sodium thiosulfate pentahydrate (STP) are underway in 2-gallon units with glycol, glycerin and acidic additives to determine effect on performance. A test loop for cycling of 45°F PCM has been constructed for test of 90 and 300 gallon bulk TES units.
Contract Number:	86X-70522V
Contract Period:	April 1, 1981 through March 1, 1982
Funding Level:	$90,207
Funding Source:	U. S. Department of Energy through Oak Ridge National Laboratory

EFFECT OF ADDITIVES ON PERFORMANCE OF HYDRATED SALT TES SYSTEMS

Calvin D. MacCracken
Calmac Manufacturing Corporation
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86X-70522V

ABSTRACT

Calmac's objectives under this contract will be to evaluate a gelling agent, developed by Calor, Ltd. of England, (1) as a means of preventing stratification in sodium thiosulfate pentahydrate and Glauber salt eutectic phase change materials; to determine techniques for the field filling and to develop repair procedures for systems incorporating the Calor gel; to study the effects of ethylene glycol and glycerin on the thermal performance of sodium thiosulfate pentahydrate and Glauber salt eutectic PCM; and to evaluate the effect of pH modification of sodium thiosulfate pentahydrate, specifically with regard to subcooling behavior.

DESCRIPTION

Calmac Manufacturing, through previous research, has gained extensive experience with the properties and performance of sodium thiosulfate pentahydrate. In fact, Calmac was successful in designing a commercially available thermal storage system, with consistently repeatable high performance, through the use of a stirring apparatus to prevent stratification. (Figure 1).

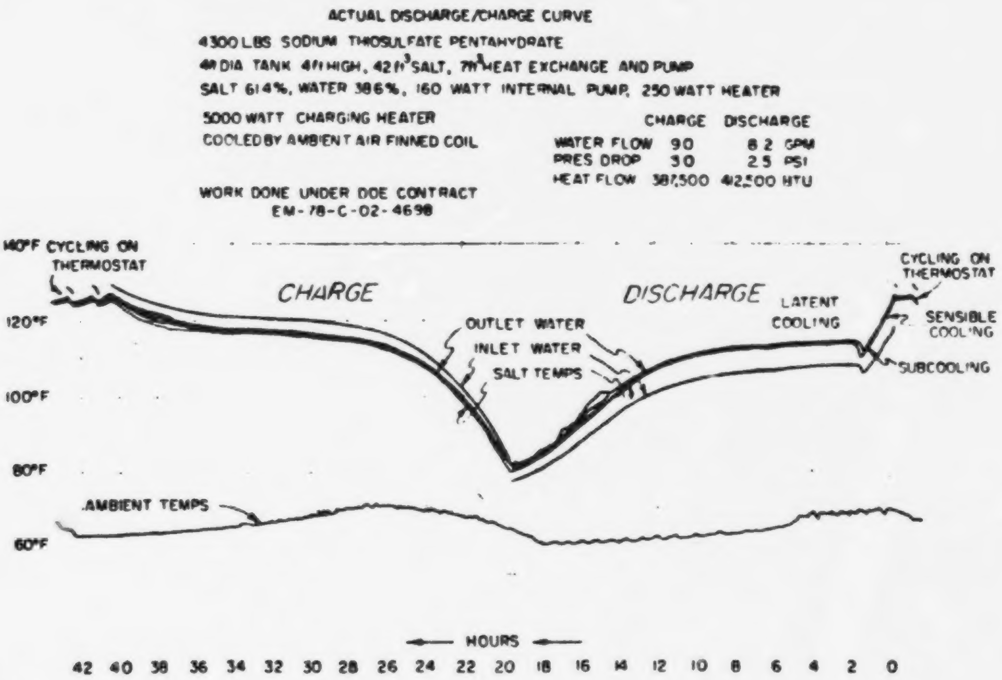

Figure 1, Typical Charge-Discharge Curve for STP with internal mechanism

However, the development of a stabilizing gelling agent offers many benefits. The cost of a stirring mechanism with associated wiring and controls would be eliminated. The absence of a mechanism within the storage tank reduces the possibility of system malfunction. Parasitic power requirements, although minimal, would be eliminated. Distortion of the heat exchanger due to buoyant forces would be controlled. Also, a gel could be used for those PCMs where a stirring pump is not successful, such as Glauber's salt and its eutectics. For this purpose, a eutectic of Glauber's salt, developed by Calmac, with a fusion point of 45°F (7.2°C) will also be tested with the Calor gel. (2).

Because of developments including the use of additives to modify the fusion point and other thermal properties of PCMs, (3) we will also study the effects of ethylene glycol and glycerin, specifically with regard to fusion point, latent heat capacity, stratification and type, rate and size of crystal growth. Also, acidic and basic pH ranges will be induced in sodium thiosulfate pentahydrate to determine the effects on thermal performance and subcooling.

All initial testing will be performed in 2-gallon containers with internal plastic tube heat exchangers which are, basically, miniature duplicates of Calmac's 360-gallon commercial units. (Figure 2) As much testing as possible regarding the effect of additives, will be done concurrently with the evaluation of the Calor gel. If the performance of the gel is less than optimal, we will hopefully be able to apply what we learn, concerning the additives, to improve the gel-PCM performance.

Figure 2, CALMAC flexible plastic tube heat exchanger

After the best possible thermal response of the gel system has been obtained in 2-gallon units, testing will then proceed to evaluation of 90-gallon units.

The Calor gel is described as a "water-insoluable hydrogel formed from a water soluable synthetic polymer having pendant carboxylic or sulphonic acid groups cross-linked with rations of a polyvalent metal (for example, aluminum or magnesium)" (1). Because this cross-linking process is fairly rapid (15-30 minutes) and transforms the gel from a pumpable liquid to a gel of semi-solid consistency, difficulties in field filling, mixing and repair of these systems is anticipated. The appropriate techniques necessary to circumvent these obstacles will be evaluated at the time testing 90-gallon units is begun.

TECHNICAL ACCOMPLISHMENTS

While we are in the early months of our contract, mixing of the Calor gel has been accomplished several variations and appears promising although a very specific field-filling procedure will undoubtedly be required. It clearly forms an extremely viscous gel which would prevent the separation previously encountered with sodium sulfate eutectics.

The addition of ethylene glycol to STP (sodium thiosulfate pentahydrate) has been found to have very specific effect on depressing the fusion temperature. This can be very helpful in adapting PCMs to solar and heat pump storage systems using warm air distribution ducts. One of the complaints of PCMs has been that they operate at one inflexible temperature.

The effect of pH on STP has been tested and appears to depend upon the crystal structure of what is used to vary the pH.

FUTURE ACTIVITIES

Calmac is, of course, a manufacturing concern. Although a comprehensive cost analysis of the TES system under investigation is not included in our statement of work, we are committed to the concept of phase change energy storage and would incorporate all viable techniques in the marketing of our already expanding line of thermal energy storage systems.

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PROJECT SUMMARY

Project Title:	Development of Advanced Heat Storage Building Materials for the Passive Solar Application
Principal Investigator:	To be determined
Organization:	To be determined
Project Goals:	To develop advanced, innovative concepts of heat storage building materials that are of demonstrated quality, reliability, and that are economically attractive.
Project Status:	The project experimental development has been initiated with the issue of a Request for Proposal in May. It is expected that multiple awards will be made soon. Theoretical analyses of the thermal response of a concrete matrix suffused with a PCM are underway and preliminary findings suggest that the thermal behavior of this material is similar to that of pure concrete with an elevated "pseudo" specific heat.
Contract Number:	To be determined
Contract Period:	To be determined
Funding Level:	To be determined
Funding Source:	U.S. Department of Energy through Oak Ridge National Laboratory

DEVELOPMENT OF ADVANCED BUILDING MATERIALS FOR THE PASSIVE SOLAR APPLICATION*

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ABSTRACT

A program to develop the concept of incorporation of phase change materials (PCMs) into conventional building materials has been initiated and consists of in-house analyses to characterize the thermal performance of a porous matrix suffused with a PCM, and concept experimental development through subcontracted efforts as the result of an RFP. The program is directed toward the development of material concepts which provide greater collection/storage efficiency and increased levels of thermal comfort in direct gain passive solar applications.

INTRODUCTION

The use of solar energy for space heating can reduce the consumption of non-renewable primary energy sources by displacing a portion of the oil and gas now used by furnaces in the building sector and by displacing fuels such as coal, nuclear, oil and gas used by central power plants which supply electricity to buildings heated resistively or with heat pumps in moderate climates.

In active solar systems, a dedicated solar collector array is placed outside of the living spaces in a building to absorb solar radiation and convert it to thermal energy. This energy can then be used for immediate space heating or can be stored for use later during periods of insufficient insolation. The fact that active collection, transport, and storage of solar energy take place away from the conditioned space, indicates that control of heat delivered to satisfy the heating demand is facilitated and can be accomplished by conventional HVAC components such as pumps, blowers, and multistage thermostats.

Passive solar systems consolidate both collection and storage functions into one assembly located in the occupied space, and use room air as the heat transport fluid. In this application, efficient utilization and control of the absorbed solar flux is a more difficult task. The collection, storage, and release of solar energy must occur within a temperature range defined by thermal comfort considerations, and be timed to interface favorably with the building heating load.

To minimize temperature fluctuations in passively heated buildings which utilize sensible heat storage, large thermal storage masses consisting of water-filled drums, or masonry walls and floor are used. Aside from the fact that these storage devices are expensive, heavy, and occupy space which could otherwise be used for living areas, the very nature of sensible TES dictates a level of overheating which at best can be reduced but not eliminated.

PASSIVE TES TECHNIQUES

Collection and storage of solar energy in passive solar applications is most commonly accomplished by one of three techniques: the mass water wall, the Trombe wall, and direct gain.

MASS WATER WALL

Water-filled drums or tubes placed behind south-facing glass can provide a collection/storage capability, and commercial products are now being sold in both new and retrofit markets. Estimates based on quotes and standard building techniques indicate that water wall storage would cost $194/m^2 ($18/ft^2) glazed area for a water storage density of 634 KJ/°C m^2 (31 BTU/°F ft^2) glazing (1). The thermal performance of water storage walls can be increased by raising the ratio of solar energy absorbed by the water to that transmitted directly into the room. In the case of clear plastic tubes, this ratio can be increased by filling the tubes with blackened water.

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A problem with water walls noted by several observers is the tendency of a water wall to immediately transfer stored energy into a room, resulting in significant room overheating during the day and underheating at night (2). This problem stems from the absence of a steep thermal gradient across the wall caused by water thermocirculation in the tubes. These undesirable temperature swings can be moderated somewhat by using water tubes of larger diameter and greater cost.

TROMBE WALL

A well-known collection/storage concept consists of a mass masonry wall several inches thick which is located adjacent to south-facing glazing as in the case of the water wall. This concept, called a Trombe wall after Felix Trombe who promoted its development and use, may be vented so that air heated in the small space between the glazing and the mass wall can circulate into the room by forced or natural convection. Thermal diffusion through the thick wall occurs slowly so that the maximum interior wall surface temperature is reached late in the evening when the building heating load is highest. This long "delay period" characteristic of a Trombe wall tempers the temperature swings in the room and provides an increased level of comfort. The fact that the solar thermal performance of a building is tied to thermal mass contained therein, does not imply that increasing the thermal mass necessarily causes an increased solar fraction. Assuming a density of 2408 kg/m^3 (150 lb/ft^3), masonry trombe walls in Albuquerque, for example, reach a performance peak at approximately 856 kg/m^2 (175 lb/ft^2) glazed area (3). This corresponds to a mass wall thickness of 36 cm (14 inches). A Trombe wall of still greater thickness provides a reduced percent solar. In terms of economics, the Trombe wall is considerably cheaper than the water wall. Estimates indicate that installed masonry Trombe wall costs would be about \$118/m^2 (\$11/ft^2) versus \$194/m^2 (\$18/ft^2) for the water wall (1).

DIRECT GAIN

The direct gain approach requires south-facing glass and thermal mass concentrated into the floor, north, east, and west interior walls, and possibly the ceiling so that the direct gain room is actually a live-in solar collector. The distinguishing characteristic of direct gain is that energy fluxes to and from storage are in opposite directions. Typically, room temperature swings in direct gain systems are larger in amplitude than that which is found in unvented Trombe wall applications. Although this large temperature swing is undesirable from the standpoint of comfort considerations, it has a positive effect on the building thermal performance. It has been shown experimentally that raising the allowable room temperature swing from ±2.8°C to ±5.6°C (±5°F to ±10°F) can increase the building solar fraction by 8% (3). Adding thermal mass can reduce these temperature swings, and results in a larger solar fraction. Unlike the Trombe wall, the addition of thermal mass in a direct gain system results in an increased solar fraction (3). Thus, the performance of a direct gain building continues to rise as the surface area of the thermal storage mass is increased, with the thickness held constant.

In an economic basis, direct gain systems compare favorably with Trombe walls. In a nationwide economic study of these two systems, in which for each square meter of glazing 1.5 m^3 of storage was allowed, it was shown that for small and large solar fractions, the direct gain system was the better economic performer (4).

In summary, water walls are the most expensive of the systems discussed, can most easily be incorporated into new or existing buildings, and effectively inhibit space temperature swings only with large storage volumes. Trombe walls are generally less expensive, difficult to retrofit, yet can provide a high degree of thermal comfort. The direct gain system is apparently the most cost effective of the three, is easily retrofitted in many cases, is capable of high solar fractions, but can cause rather large space temperature swings. In addition, considerable flexibility exists in storage location in direct gain systems in that the storage capability resides in conventional architectural components (walls, ceiling, floor) thereby affording them a dual function capacity.

PHASE CHANGE MATERIALS IN PASSIVE SOLAR

The use of a phase change material (PCM) for latent heat storage in passive solar applications could bring certain qualities to direct gain passive systems which reduce the uncomfortable temperature swings associated with sensible heat storage in passively heated buildings, and permit a reduction in storage weight and space. Latent heat storage is more nearly isothermal in nature than sensible heat storage in that energy fluxes to and from the material take place over a narrow temperature range centered around the PCM melting point. Therefore, a PCM incorporated into a passive solar heating system would tend to reduce room temperature swings. Furthermore, the PCM would provide a storage density greater than that of sensible heat storage over an acceptable temperature range in water or masonry. Experimental investigations using PCMs in passive solar applications have provided evidence which support these arguments. In an experiment using small greenhouses, storage walls containing calcium chloride hexahydrate were compared with walls containing water. Recorded temperatures showed that the latent heat wall collected solar energy with greater efficiency and stored twice as much heat as a water wall of the same volume, while acting as a very good temperature filter by minimizing temperature swings within the enclosed room (5). An experimental comparison between a PCM (calcium chloride hexahydrate) wall and a masonry wall have shown that the 7.6 cm (3 inch) thick PCM wall demonstrated slightly better thermal performance than a masonry wall five times as thick (6). Thus, the evidence to date supports the contention that PCMs combined with passive solar storage are a promising match.

PROGRAM PLANS AND PROGRESS

During FY 1981, a program to study and develop building materials containing PCMs for direct gain applications has been initiated. The work is progressing along two parallel paths. The first consists of laboratory-scale, experimental concept development through subcontracts. The second path follows several branches consisting of in-house analyses of the thermal behavior of walls suffused with a PCM, development of a simplistic approach to the moving boundary problem in a wall, and utilization of this simplistic model to characterize the global thermal performance characteristics of a passive structure using the building energy analysis computer code, DOE-2.1. DOE-2.1 requires that specific heats and thermal conductivities of those building components which interact thermally be given, allowing the program algorithms based exclusively on sensible heat storage to predict building performance. To use the program in the anlysis of latent storage requires an affirmative answer to the following question: "Can the thermal performance of a latent storage wall be reasonably well approximated by that of a sensible storage wall with an elevated, "pseudo" C_p? Preliminary investigations have revealed that the question can be answered in the affirmative (7). These results indicate the thermal performance of a storage wall consisting of a 50% by volume mixture of concrete and calcium chloride hexahydrate may be approximated by sensible heat storage in concrete with a "pseudo" $C_p \cong 6$ cal/gm°C. Although these results are preliminary, they serve to point out the disparate nature of sensible and latent storage characteristics and indicate the limitations of conventional sensible heat storage in existing materials.

The experimental program was initiated in May through the release of a Request for Proposal (RFP). The RFP called for a three-phase plan of action to propose, develop, and test a PCM/building material concept. Phase I of the effort consists of development and testing the concept on a laboratory scale, an applications study, and economic analysis. Phases II and III require the fabrication, testing and analysis of full scale "modules" as determined by the specific concept. There has been a favorable response to the RFP, and it is expected that awards will soon be made for the Phase I effort.

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PROJECT SUMMARY

Project Title: Assessment of Energy Storage for Solar Applications

Principal Investigators: Dr. David J. Edwards and Solomon Rosenzweig

Organization: The Aerospace Corporation
20030 Century Boulevard
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Project Goals: To assess the technical and economic viability of energy storage in near-term solar energy systems, thereby providing information by which research and development programs can be formulated. The Aerospace Corporation is coordinating the work of Brookhaven National Laboratory, Sandia National Laboratories/Albuquerque, and the Solar Energy Research Institute, who are in the process of assessing the performance characteristics and requirements of energy storage for solar energy applications.

Project Status: The study is being conducted in five phases, of which the first three are complete:

1. The conduct of a survey of solar energy applications to determine potential roles for energy storage systems and to select application areas for emphasis.
2. The development of a uniform methodology for assessments to ensure a valid basis of comparison of energy storage systems within a particular application.
3. The preparation of a summary of prior assessments applicable to the energy storage applications defined in Phase 1.
4. The evaluation of existing assessments, summarized in Phase 3, and the conduct of additional assessments as required.
5. The preparation of recommendations for further solar energy storage research and development programs based on the results of the assessments conducted in Phase 4.

The fourth phase is currently underway. The fifth phase will result in recommendations for research and development programs by September 1981.

Contract Number: IPR-EM-78-01-5217

Contract Period: FY 79-81

Funding Level: $560K

Funding Source: Office of Energy Systems Research, U.S. Department of Energy

ASSESSMENT OF ENERGY STORAGE FOR SOLAR APPLICATIONS

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ABSTRACT

An overview of the first three phases of the Solar Applications Analysis for Energy Storage study performed for the Office of Advanced Conservation Technologies of the Department of Energy is presented. Phase 1 surveyed solar energy applications, Phase 2 developed a uniform methodology for assessments, and Phase 3 summarized prior applicable storage assessments. Three referenced reports thoroughly cover each of the phases and are available from the authors.

INTRODUCTION

The Aerospace Corporation is coordinating a multilaboratory study for the Office of Energy Systems Research, the objective of which is to assess the technical and economic viability of energy storage in near-term solar energy applications. Near-term applications are those having the potential for significant market penetration by the year 2000. The results of the study will assist the Department of Energy, Office of Energy Systems Research, in formulating its research programs to meet national needs. The study is being accomplished in five phases:

Phase 1: A survey of solar energy applications to determine potential roles for energy storage systems and to select application areas for emphasis

Phase 2: The development of a uniform methodology for assessments to ensure a valid basis for comparing energy storage systems for a particular application

Phase 3: The preparation of a summary of prior storage assessments applicable to the energy storage applications defined in Phase 1

Phase 4: The evaluation of existing assessments, summarized in Phase 3, and the conduct of additional assessments as required, based on the results of Phase 3 (to be accomplished by the Department of Energy national laboratories and the Solar Energy Research Institute)

Phase 5: The preparation of recommendations for future energy storage research based on the results of the assessments conducted in Phase 4.

This paper discusses the results of the first three phases of the study. The fourth phase is currently being conducted. The fifth phase is scheduled to be completed by the end of September 1981.

SELECTED APPLICATIONS

The survey of solar energy applications to determine potential roles for associated energy storage systems resulted in the selection of five applications as candidates for assessment. The five applications originally* selected and the organizations performing the analysis are as follows:

- Agricultural and industrial process heat -- active solar thermal energy source - Solar Energy Research Institute
- Residential and commercial space heating/cooling and hot water -- active solar thermal energy source - Solar Energy Research Institute
- Electricity for central/community applications -- wind energy source - Sandia National Laboratories/Albuquerque
- Electricity for central/community applications -- photovoltaic energy source - Sandia National Laboratories/Albuquerque
- Residential, commerical, and light industry space heating and cooling -- passive solar thermal energy source - Brookhaven National Laboratory

The selection process was accomplished in three steps: (1) matrix evaluation, which was accomplished by a small working group coordinated by Aerospace; (2) review by the Office of Energy Systems Research, who independently performed the matrix evaluation; and (3) comparison by Aerospace with the Domestic Policy Review of Solar Energy. The first step involved the development of a set of matrices of potential solar energy applications/energy storage technologies. These matrices were developed to screen all possible combinations of solar and storage technologies with the intent of identifying those combinations that could possibly satisfy near-term national energy goals. This implies either state-of-the-art technology or technology that could be developed by 1985. The applications were then evaluated according to their potential for meeting the goals, which resulted in 26 solar/storage applications with significant potential.

The second step consisted of obtaining the opinions of the Office of Energy Systems Research technical staff regarding which solar applications would require further analysis from a storage point of view. Eight of these 26 applications were judged by the staff to have significant potential.

The third step was a review of the Domestic Policy Review of Solar Energy and its interpretation as provided in the Draft DOE Policy, Programming and Fiscal Guidance, FY 1982-1986, January 30, 1980. In comparing the Domestic Policy Review high-potential solar applications with the staff recommendations, six applications were seen to be common to both. From these, four applications were chosen for further analysis in FY 1981. Solar thermal energy for space heating of buildings was divided into passive and active systems, which brought the number of applications for study in FY 1981 to five, as defined previously. The details of the Phase 1 study are presented in "Selection Rationale for High-Value Solar/Energy Storage Applications."[1]

UNIFORM ASSESSMENT METHODOLOGY

The objective of Phase 2 was to develop a uniform methodology to ensure that the assessments done in Phase 4 are completed on a common basis. This has been accomplished by delineating both the governing assumptions and the figures of merit to be used in the assessments. The major governing assumptions include the specification of the regional data; the energy forecast scenarios; and the standards for cost estimating, including economic and financial calibration values. The details of this methodology are presented in "Uniform Assessment Methodology for Energy Storage Applications."[2]

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* The two central/community applications were dropped because previous assessments had shown that storage dedicated to the energy source was not the best way to proceed. These were replaced by electricity for building services, whose energy source is wind or photovoltaics.

System Methodology

The overall system methodology flow, as indicated in Figure 1, basically optimizes a system first without, then with, energy storage. The assessment is initiated with the selection of the solar application and the identification of the candidate energy conversion technologies and the associated storage systems to be considered for that application. The analysis is performed for one or more of several different energy and economic scenarios and one or more Typical Meteorological Year cities.

The energy and economic scenario chosen provides input values for a range of energy and economic parameters. The choice of a particular scenario implies acceptance of the driving assumptions of that scenario. Specifically, the use of a high world oil price (the high scenario) carries with it assumptions concerning the prices of alternative fuels, the availability of alternative fuels, and the projected level of economic activity over the next 15 years. Included in the scenarios are projections for the price of electricity, gas, and other fuels used to generate electricity and assumptions about the particular time-of-day pricing structure, the prevailing discount rate, the financial structure for a homeowner application, the prevailing property tax rate, the income tax rate, salvage values, and other nonregional components of the analysis. A number of highly regionalized values are also selected, including regional fuel prices; system-specific cost values, such as capital cost per kilowatt; operation and maintenance costs; and other elements that would be used in defining the stream of life-cycle costs. All of the aforementioned parameters are used to estimate the benefits and costs of the application on a with- and a without-storage basis for both stand-alone and grid-connected applications. The various markets that might conceivably install the device (homeowners, regulated utilities, unregulated industry, or government) all have different figures of merit by which they would assess the value of including storage capacity in the application.

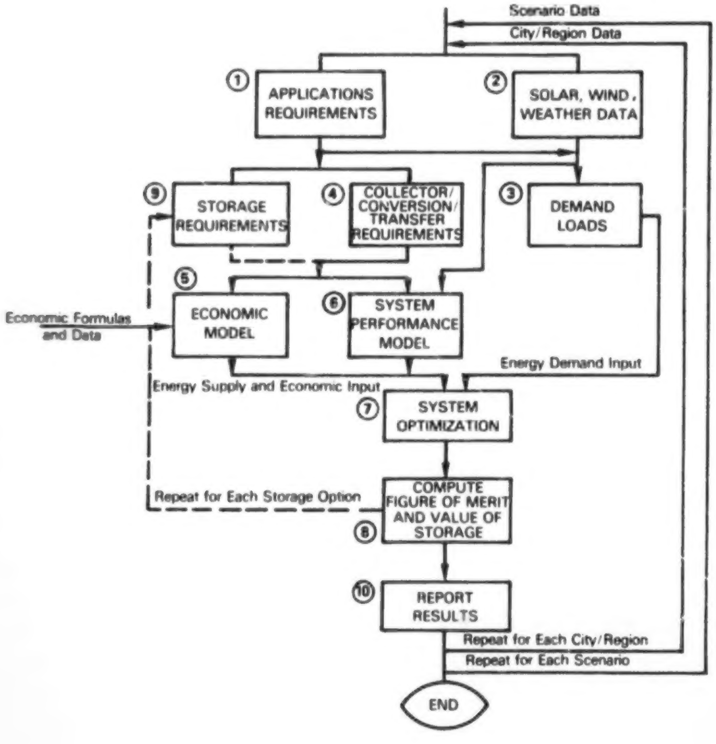
Scenario Data
City/Region Data
① APPLICATIONS REQUIREMENTS
② SOLAR, WIND, WEATHER DATA
⑨ STORAGE REQUIREMENTS
④ COLLECTOR/ CONVERSION/ TRANSFER REQUIREMENTS
③ DEMAND LOADS
⑤ ECONOMIC MODEL
⑥ SYSTEM PERFORMANCE MODEL
Economic Formulas and Data
Energy Demand Input
Energy Supply and Economic Input
⑦ SYSTEM OPTIMIZATION
Repeat for Each Storage Option
COMPUTE FIGURE OF MERIT AND VALUE OF STORAGE ⑧
⑩ REPORT RESULTS
Repeat for Each City/Region
Repeat for Each Scenario
END

Figure 1. System Flow

Standardization of Regional Data

The selection of standardized solar, wind, and weather data is based on the examination of three candidate data bases: the Test Reference Year, the Westinghouse-SOLMET year, and the Typical Meteorological Year. Each of these data bases was examined in some detail, resulting in the selection of the Typical Meteorological Year data for use in this study. It not only considers radiation, but also wind, temperature, and humidity.

Energy Forecast Scenarios

The Energy Information Administration, a component of the Department of Energy, is responsible for processing and publishing data on energy reserves, production, demand, consumption, and the financial status of energy-producing companies. Both the Federal Energy Administration Act of 1974 and the Energy Conservation and Production Act of 1975 require that the Administration prepare an annual forecast of energy production and consumption in the short-, mid-, and long-term periods. These forecasts are published as part of the Administration's annual report to Congress. The Administration energy projections should be incorporated in assessments of the value of solar energy storage because (1) they are the official Department of Energy projections, (2) they include a broad range of scenarios that are broadly accepted, and (3) the energy equilibrium model used is multiregional.

Economic and Financial Calibration Values

The economic and financial calibration values are generally given as ranges of parameters, including one calibration value that will be used in future assessments to calibrate results from assessment to assessment. These values and ranges are presented in Section 5 of the methodology report.[2]

Figures of Merit

A single standard measure of system performance is required as a guide to the optimization of the system design. Many technical measures of performance are available; however, their optimization criteria are usually mutually exclusive. Therefore, an economic figure of merit is used as the objective function for optimization in this analysis. The economic figure is a measure of the relative value of the system from the perspective of the potential purchaser. It includes an implicit weighting of the technical performance criteria as they affect the value.

The energy systems are evaluated from the perspective of four application sectors:

- Homeowners
- Commercial and industrial firms
- Privately owned, regulated utility firms
- Government

The system optimization is based on a single figure of merit. Further analysis of the system, however, may require other figures of merit representing particular aspects of the system in each application. This is analogous to the situation that will be faced by the manufacturers of these systems. They will have to standardize the systems according to some general market guidelines in order to realize the economies of large-scale production. Having done that, they may promote the systems in different market segments according to the features that are most desirable to those segments.

The figures of merit developed in this analysis differ among the application sectors. These figures include those most commonly used in energy system studies, but the list is not exhaustive. Some studies may develop additional figures of merit, although the figures described in this analysis should be common to all future studies to ensure comparability of the results. The first named figure of merit was used in the optimization procedure, and the remaining were calculated based on that optimized system.

Application Sector	Figures of Merit
Homeowners	Net Present Value Benefit/Cost Ratio Initial Cash Outlay Payback Period
Industry	Net Present Value Benefit/Cost Ratio Internal Rate of Return Payback Period
Utilities	Net Present Value Benefit/Cost Ratio
Government	Net National Economic Benefit

The following is a typical calculation of a figure of merit equation for homeowner life cycle cost.

$$LCC = DP - ITC_{PV} - SV_{PV} + RC_{PV} + LP_{PV} + FP_{PV} - ES_{PV} + OM_{PV} + PT_{PV}$$

VARIABLE	DESCRIPTION
LCC	Life Cycle Cost
DP	Down Payment
ITC_{PV}	Present Value of the Initial Energy Investment Tax Credit
SV_{PV}	Present Value of the Expected Salvage Value
RC_{PV}	Present Value of Future Component Replacement Costs
LP_{PV}	Present Value of Loan Payments
FP_{PV}	Present Value of Fuel and Electricity Purchases
ES_{PV}	Present Value of Electricity Sold Back to Utility
OM_{PV}	Present Value of Operations and Maintenance Expenses
PT_{PV}	Present Value of Property Taxes

This analysis does not treat the Federal Government as a separate application sector for which solar energy or storage systems will be simulated and optimized. Rather, the Government assesses these systems from a national resource use perspective by examining the simulated actions of the private decisionmakers in the other sectors. For this purpose, a net national economic benefit (NNEB) equation is specified. This equation is not used for system optimization, but is an alternative figure of merit. NNEB summarizes the economic benefit and cost of the energy systems as they affect the Nation as a whole, without regard to which individuals the benefit and cost accrue. NNEB differs from the figures of merit for the other sectors in several aspects, as follows:

- NNEB excludes taxes, subsidies, and other intranational transfer payments.
- For NNEB, the discounting of future benefits and costs occurs at the social rate of discount rather than the private cost of capital.
- For NNEB, all costs are measured at the marginal resource cost to the Nation rather than at the prices faced by the application sectors.

SURVEY OF PRIOR ASSESSMENTS

Twenty-eight prior solar energy storage assessments applicable to the current study were identified by surveying the personnel of the Department of Energy national laboratories and the Solar Energy Research Institute. Each of the laboratories was asked for valid, accepted reports on energy storage requirements and capabilities for solar energy systems. Ten reports related to the five selected applications designated in the Phase 1 report are reviewed and summarized in "Survey of Energy Storage Assessments for Solar Applications."[3] It was not the objective of Phase 3 to determine the value of these assessment reports to the study, but to provide a basis for the national laboratories and the Solar Energy Research Institute to determine the validity of the assessments when compared to the uniform set of criteria and assessment methodology developed in Phase 2.

To standardize the presentation of technical and economic data, a common set of parameters was developed, against which each assessment was compared. First, the objectives, assumptions, methodology, and conclusions of each assessment were summarized.

Next, the energy storage system performance and technical characteristics included in each of the assessments were reviewed to determine the degree to which the following parameters were addressed:

- Energy storage capacity
  - (capacity rating) (MWh)
- Power rating (MW)
- Duty cycle (cycles/yr)
- Charge/discharge time
  - Charge (hr)
  - Discharge (hr)
- Storage efficiency (%)
- Lifetime (yr)
- Temperature range (°C)
- Energy density
- Thermal storage
  - Specific heat (Btu/lb °F)
  - Latent heat (Btu/lb)
- Reliability
- Maintainability
- Safety
- Environmental effects
- Material scarcity
- Institutional factors
- Geographic locales
- Solar fraction

Finally, the assessments were reviewed with respect to eight major cost and economic parameters:

- Fuel price
- Borrowing costs
- Taxes
- Solar system costs
- Energy storage system costs
- General economic factors
- Cost goals
- Figure of merit

These lists were developed from data used in various assessments and include those parameters described in the methodology report.[2] These factors, as appropriate or available, were identified for each assessment that was reviewed and are listed in the summary reviews presented in the survey report.[3] The reviews determined that the various assessments did not use a common set of parameters. Also, for a given solar energy application, the methodology of evaluation used was different, due to the several methodologies available. This is not a criticism of the reports, for each report had a different goal. It is hoped that some of the data presented in these reports will be useful for Phase 4; however, because no common data base or methodology was used, a comparison of the assessments was impossible at that time. Phase 4 will apply a common data base and methodology within a solar energy application so that a valid comparison of storage technologies can be made.

Another point to be noted is that not all applicable energy storage technologies were considered for a given solar energy technology. Phase 4 will examine and optimize the various storage technologies considered most applicable (in Phase 1) to the solar energy application.

A final point resulting from this review was that regional considerations in the assessments did not overlap to any great extent. Phase 4 will use a common set of regions with a common set of input data.

ADDITIONAL ASSESSMENTS AND RECOMMENDATIONS

The additional assessments called for in Phase 4 are presently being conducted by the Brookhaven National Laboratory, the Sandia National Laboratories/Albuquerque, and the Solar Energy Research Institute. The recommendations for energy storage research will be made in Phase 5 after the completion of Phase 4.

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2. The Aerospace Corporation, "Uniform Assessment Methodology for Energy Storage Applications," Report 80-520, D.J. Edwards, December 1980.

3. The Aerospace Corporation, "Survey of Energy Storage Assessments for Solar Applications," Report 80-524, M.R. Harper, December 1980.

PROJECT SUMMARY

Project Title: Modeling the Moving Boundary Problem for TES with PCMs

Principal Investigator: Ralph M. Deal

Organization: Chemistry Department
Kalamazoo College
Kalamazoo, Michigan 49007

Project Goals: Experimental and theoretical modeling of the moving boundary problem in phase change materials used in thermal energy storage.

Project Status: Two initial phases have been completed.

Implementation of a simple graphics demonstration of temperature profiles for a melting PCM based on both an analytical solution and a Budak numerical solution for a one-dimensional slab.

The determination of the range of validity and optimal parameter criteria for the use of the Budak method for modeling heat transfer in PCMs.

Contract Number: UCND 9038

Contract Period: April 1, 1981 through September 30, 1982

Funding Level: $41,613

Funding Source: U.S. Department of Energy through Oak Ridge National Laboratory

MODELING HEAT TRANSFER IN PCM'S WITH THE BUDAK METHOD

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ABSTRACT

A simple numerical procedure for calculating the flow of heat in a one-dimensional phase change material developed by Budak has been tested against an analytical solution to determine the best choice of parameters for a range of Stefan numbers. Simple rules are provided by which an inexperienced user of the method can obtain reasonably reliable results for a simply melting substance.

INTRODUCTION

The Budak method as described by A.D. Solomon allows rapid numerical solutions for the temperature at node points in a one-dimensional model of a PCM as a function of time with no explicit designation of nodes at the melting/freezing front. This method introduces some approximations which can lead to quite inaccurate results if not used properly. Systematic testing of the method for a range of Stefan number against an analytical solution provided data for devising a set of rules for selecting parameters for new PCMs and Stefan numbers.

THE BUDAK METHOD

The method as described by Solomon in reference 1 consists of smearing the melting process over a range of temperatures such that the usual heat equation,

$$C\rho T_t = (kT_x)_x \tag{1}$$

works throughout the change from one phase to the other. This is achieved by defining a temperature range extending either side of the critical temperature through which the heat capacity of the PCM is defined to give an apparent sensible heat over that temperature range equal to the latent heat for the phase transition. That is, the heat capacity is defined differently over three temperature ranges:

$$\begin{gathered} C(T) = C_s \text{ for } T < (T_{cr} - \varepsilon_s) \\ C(T) = C_1 \text{ for } T > (T_{cr} + \varepsilon_1) \\ C(T) = H/(\varepsilon_s + \varepsilon_1) \text{ for } (T_{cr} - \varepsilon_s) < T < (T_{cr} + \varepsilon_1) \end{gathered} \tag{2}$$

where C_s is the heat capacity for the solid, C_1 is the heat capacity for the liquid, ε_s is that portion of the "melting range" below T_{cr}, and ε_1 is the portion above T_{cr}.

The other thermal properties must be defined so that they have proper values at the edges of the "melting range". The main finite difference equation used in calculating the temperature at a node in the PCM is

$$T_j^{n+1} = T_j^n + [\delta t/(C\rho\delta x^2)][K_{j+}^n(T_{j+1}^n - T_j^n) - K_{j-}^n(T_j^n - T_{j-1}^n)] \tag{3}$$

where n is the prior time index, n+1 the current time index, j is the node position index, K_{j-} and K_{j+} are calculated as means for the K values appropriate for the temperatures of the nodes on either side of the left (j-) or right (j+) boundary of the jth node. K then has one of 5 values, the first and 5th being K values for the liquid and solid phases. C is the heat capacity based on the temperature of the jth node at time n. This equation is essentially that described by A.D. Solomon in reference 1.

IMPROVEMENT IN THE BUDAK METHOD

One of the difficulties in the Budak method is that sensible heat is lost for the range of temperatures extending either side of the critical temperature in the "melting range". That was simply corrected in the program developed to implement the Budak simulation by changing the equation for the heat capacity over the range:

$$(T_{cr}-\varepsilon_s) < T < (T_{cr} + \varepsilon_1) \quad \text{to}$$

$$C(T) = (H + \varepsilon_s C_s + \varepsilon_1 C_1)/(\varepsilon_s + \varepsilon_1) \tag{4}$$

where the sensible heat lost is simply added to the latent heat. This modification works well and can make a noticable difference for large "melting ranges".

PROGRAM DEVELOPMENT

Both the program used to obtain analytical solutions for comparison and the program to implement the Budak method were written in PASCAL on an APPLE II microcomputer with interactive graphics. Most of the longer runs used to develop the recommendations were on a PDP-10 at Western Michigan University to which the PASCAL programs were transferred.

RECOMMENDATIONS FOR CHOICE OF BUDAK PARAMETERS

The rule of thumb developed for the use of the Budak method has in mind a user who wants to calculate the temperature profiles over time for some anticipated application of a PCM for TES where the thermal properties of the PCM are known for both phases, as well as the particular temperature range over which he/she expects to use the PCM. In the tests performed so far, the material is assumed to be solid at the critical temperature and to have one face of a slab suddenly raised to a constant temperature above the critical temperature. In this case the Stefan number is well defined as

$$C(T_{face} - T_{cr})/H \tag{5}$$

The analytical solutions for this problem presented by Carslaw and Jaeger in reference 2 were used to check the accuracy of several runs at each of several Stefan numbers ranging from 0.50 to 1.25. The recommendations developed fot this range of Stefan numbers are currently being checked over a wider range and further comparisons being made with the more general analytical solution provided by Carslaw and Jaeger for the case of the initial temperature being lower than the critical temperature. There are no obvious reasons why the recommended parameter selection procedure will be different for these less restricted cases.

The goal in developing these recommendations was to use minimal computer time for a reasonable fit to the correct solution. The assumption is that procedures developed under these circumstances are applicable even in circumstances where there are no analytical solutions. In any case, the most severe conditions are when the temperature of the face is suddenly changed with respect to the temperature of the PCM next to the face causing a phase change in the PCM. Under those conditions, it is very easy for a node to "pop" out of the "melting range" before the full latent heat has been absorbed.

The analytical solution is for a semi-infinite slab whereas the Budak simulation is for a finite slab. This did not prevent considering the analytical solution as the correct solution since many nodes in the finite model were still very close to the initial temperature at the end of the test runs.

The recommendations are as follows:

1. Calculate the Stefan number for the proposed application.
2. Calculate the thermal diffusivity from the thermal properties. The value for liquid phase was used in the tests since the temperature changed only for that phase.
3. For a reasonably close fit to a correct solution, the Budak parameters for the time step,

δt should be:

$$\delta t = \delta x^2/(8\alpha) \tag{6}$$

and the "melting range",

$$\varepsilon = StH/(3.2C) = \Delta T/3.2 \tag{7}$$

The parameter choice given was for a fit of one to three percent to the temperatures after the first few nodes have "popped" out of the "melting range". Up to 4 times greater values of dt will still be stable in the numerical iterations but lead to excessive deviations from correct temperatures.

Smaller δt values will of course lead to more accurate results but require that much more time. For example, if a better fit is desired, the next set of recommendations are:

$$\delta t = \delta x^2/(16\alpha) \tag{8}$$

and

$$\varepsilon_1 = StH/(4.8C) \tag{9}$$

CONCLUSION

The Budak method is a simple useful method for simulating the transfer of heat by pure conduction in one dimension. With the use of the recommended parameters, a relatively inexperienced user can expect to get results useful for prediction of the behavior of a PCM in a projected TES application.

REFERENCES

1. A.D. Solomon and C.E. Serbin, TES - A Program for Simulating Phase Change Processes, ORNL/CSD-51, 1979.

2. H. Carslaw and J. Jaeger, Conduction of Heat in Solids, Oxford at the Clarendon Press (1959).

PROJECT SUMMARY

Project Title: Survey of Commercial Thermal Storage Installations in the United States and Canada

Principal Investigator: Dr. Harold G. Lorsch

Organization:
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Project Goals: To determine the type and number of commercial thermal storage installations that are in existence, and to list their major technical characteristics. To have this information published as a special document by ASHRAE. To describe six representative installations in detail.

Project Status: The initial survey was completed. The technical report draft which contains the results of the survey was reviewed by an ASHRAE Technical Evaluating Committee. Based on their recommendations, the report is being revised and, at the same time, information on additional installations is being added. The revised report will be published and distributed by ASHRAE.

Tentative selections of representative installations to be described in greater detail are being made subject to UCC approval.

Contract Number: BOA-41B-28915C-41Y-01

Contract Period: July 2, 1980 through December 31, 1981

Funding Level: $85,288

Funding Source: U. S. Department of Energy, Division of Energy Storage Technology, through Union Carbide Corporation Nuclear Division

SURVEY OF COMMERCIAL THERMAL STORAGE INSTALLATIONS IN THE UNITED STATES AND CANADA

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ABSTRACT

Nearly 300 thermal energy storage installations in the United States and Canada were identified by a mail and telephone survey conducted by the Franklin Research Center. Information was obtained on approximately 220 installations. For 175 installations of hot, cold, and combination hot/cold storage, sufficient quantities of technical information were obtained to warrant inclusion in the report. Water is the most prevalent medium of energy storage. Although almost all respondents indicated satisfaction with the performance of their storage systems, hardly any could provide detailed performance records. Operational and construction cost data were either unobtainable or were not specified sufficiently to be useful. The project is continuing in two phases: publication of the survey data by ASHRAE, and development of detailed descriptions as well as performance and cost data for six representative installations.

SCOPE

A survey of commercial thermal energy storage installations in the United States and Canada was undertaken by the Franklin Research Center (FRC) on behalf of the U.S. Department of Energy acting through the Oak Ridge, TN facility of the Union Carbide Corporation, Nuclear Division. Mr. James Martin was the Project Monitor.

The survey was to include both hot and cold storage projects but was to exclude experimental systems, domestic hot water storage, storage primarily used for solar energy, and storage in one- and two-family homes. Off-peak ice storage used in churches, dairies, and breweries was also excluded from the survey. No site visits were undertaken.

OBJECTIVE

Many people consider thermal energy storage to be in an experimental stage. To show that this is no longer the case, this survey was undertaken, and its results will be published for the benefit of design professionals, building owners and operators, and utility personnel. It provides locations of thermal storage installations, system details, and information about their performance. The names, addresses, and telephone numbers of persons familiar with each installation are also given for the benefit of those who wish to obtain additional information.

The purpose of this survey is to document the extent of thermal storage application, its reliability, and its versatility. It is hoped that it provides useful examples of successfully executed projects, and that it will induce others to apply thermal storage under suitable conditions.

METHODOLOGY

Potential information sources were located in several ways. Thermal storage projects known to FRC personnel through their activities in the thermal storage area were searched out. Design engineers who had designed and/or built thermal storage systems were contacted.

The Principal Investigator, in his capacity as the founder and chairman of the ASHRAE Technical Committee on Thermal Storage, was familiar with engineers throughout the HVAC industry and with electric utility personnel who had an interest in the subject. Several volumes of the Survey of Utility Load Management and Energy Conservation Projects, references 1 and 2, were used to identify electric utilities that had been and are active in promoting thermal storage. The Electric Power Research Institute and the Edison Electric Institute were also contacted to supplement this list.

A survey on chilled water storage facilities had been undertaken on behalf of the Southern California Edison Company by Marx Ayres Associates, reference 3, and it was made available to this project. Manufacturers of thermal storage devices also provided leads to a number of projects.

The bulk of the information was obtained by telephone and through questionnaires sent to follow up phone calls. "Cold" mail questionnaires were found to be useless. In many cases, the initial phone call was sufficient to obtain the required information; in other cases, follow-up calls were required. When the individual contacted could not immediately make the time available to answer questions, a follow-up call was made, or a letter including copies of the survey form was sent. Information relating to other installations was always encouraged. Frequently, individuals contacted about one project knew of additional sites and/or had knowledge of other engineers who had executed thermal storage projects. These leads were then followed up.

In most cases, a number of telephone calls was required before reaching the person who had the information desired. Thus, the number of telephone calls made for this survey is approximately one-thousand, the total number of letters written is approximately one-hundred and fifty.

The results of the thermal storage survey will be published by ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) in a special document. The society expressed its willingness to do so provided ASHRAE had some inputs to the contents and format of the document. This input was obtained through a three-member ASHRAE Technical Evaluating Committee which met twice with FRC personnel and made recommendations that are being carried out. Publication is planned for later in the year (1981).

RESULTS AND DISCUSSION

Close to 300 installations in the United States and Canada have been identified. It is believed that this covers between 50% and 90% of the installations that actually exist in that area. Some technical information was obtained on 220 installations. Sufficient information to draw preliminary conclusions is available for 175 at the present time.

The overwhelming majority of the thermal storage installations identified perform satisfactorily. Less than five percent of the respondents indicated significant problems, such as the break of an electrical cable embedded in a concrete floor, excessive thermal response time, or lack of set-point temperature stability. However, documented performance records are virtually non-existant. In the majority of cases, the owners or designers merely indicated their estimates or their opinions as to the performance of the systems without having any measured data to back up their claims. Only a handful of operators were able to quantify the actual energy impact which thermal storage has upon the overall performance of their systems.

The performance of the retrofit systems was equally satisfactory, according to the owners' reports. Unfortunately, the majority of the retrofit systems were introduced in connection with a modification or enlargement of the original installation; therefore, a simple comparison between "before" and "after" energy consumption or cost data is not possible.

Of the 175 installations on which sufficient data are available, 58% are heat storage systems, 23% are cold storage systems, and 19% are combined heat and cold storage systems. A summary of system applications by geographic regions is shown in Table 1.

Table 1. Geographic Distribution of Systems by Application

Region	Heat Storage	Cold Storage	Heat and Cold Storage	Total
United States				
Northeast	38	6	17	61
Northwest	0	0	1	1
Southeast	10	2	3	15
Southwest	4	15	1	20
Midwest	28	7	9	44
Canada	21	10	3	34
TOTAL	101	40	34	175

The table shows that:

- Heat storage predominates in the East, the Midwest and Canada,
- Cold storage predominates in the Southwest,
- The Northeast has a relatively high degree of combination heat and cold storage systems,
- Storage is virtually non-existant in the Northwest.

A breakdown by storage medium, storage system, and country is given in Table 2. The preferred storage medium for hot storage is water (62%) followed by sand (29%), and brick and concrete (9%). Two-thirds of the water storage installations use pressurized water with the storage temperature above 100°C. In the United States, ice is the preferred storage medium over chilled water by 2:1, but no ice storage installations were found in Canada. Water predominates (82%) in the combined heat and cold storage installations; a few U.S. installations use the sensible heat of water for heat storage and the latent heat of the water/ice transformation for cold storage. Only further investigations will allow a definitive analysis of whether this apparent trend in thermal storage system type and distribution is due to basic geographic and climatic considerations or is caused by rate structures, hardware availability, or other economic considerations.

Table 2. Storage Media and Systems by Country

Storage Type	United States	Canada	Total
HEAT STORAGE			
Pressurized Water (> 100°C)	27	15	42
Unpressurized Water (< 100°C)	16	5	21
Sand	29	0	29
Concrete, Brick	8	1	9
COLD STORAGE			
Water	10	10	20
Ice	20	0	20
COMBINED HEAT AND COLD STORAGE			
Water	25	3	28
Water/Ice*	6	0	6
TOTAL	141	34	175

*Water is used for heat storage, ice for cold storage

The reasons for the installation of thermal storage systems are shown in Table 3.

Table 3. Stated Reasons for Installing Thermal Storage Systems

Region	Peak Demand Reduction	Off-Peak Rates
United States		
Northeast	36	23
Northwest	1	0
Southeast	12	1
Southwest	20	0
Midwest	25	16
Canada	34	0
TOTAL	128	40

Demand reduction offers the most attractive financial incentive for substantial cost savings arising from thermal storage. Since demand charges are levied for at least the length of the billing period and, in many cases, for the better part of a year (demand ratchet tariffs) even though the duration of that peak demand may be relatively short, the use of thermal storage to reduce these peaks is highly beneficial. Reduced off-peak energy rates were offered by relatively few utilities in the past, notably in the Northeast and the Midwest, although this may be changing due to recent legislation, such as PURPA.

MARKETING

Marketing of thermal storage systems involves the electric utility as a prime actor with manufacturers and design engineers as secondary actors. All of them are needed, however, if the promise of conservation through thermal energy storage is to be fulfilled. An aggressive marketing campaign by a manufacturer can have a significant impact on the utility and, in some cases, on its policies if the economics are favorable to thermal storage. Suitable rate structures as well as the availability of utility staff and support can provide a marketing impetus to thermal storage systems that is beneficial to the utility and its customers.

In general, electric utilities are the prime movers in the application of thermal storage. They make its use economical and attractive through proper rate structures. This is apparent from the survey which shows concentrations of thermal storage installations in the service areas of certain utilities, while no thermal storage is used in neighboring utility service area with, presumably, similar environmental conditions.

CONCLUSIONS

The majority of building owners and operators are highly satisfied with their thermal storage systems, although few are able to provide hard data to back up their "gut feelings". The operational performance of thermal storage devices is excellent; very few cases of unsatisfactory operation were reported.

The reduction of peak demand is the preponderant reason for installing thermal storage. Lower off-peak energy rates are the reason in only 20% of the installations. Electric utilities provide the major impetus to the installation of thermal storage. One should therefore look to the electric utility industry as the major vehicle for wider use of thermal storage.

There exists a large quantity of qualitative performance data on thermal storage, but few quantitative performance and cost data. The performance of thermal storage installations is rarely monitored because monitoring appears to be an unnecessary expense to the building operator. If reliable, long-term performance data are desired, an outside agency must inaugurate a separate program to that effect.

Financial information on thermal storage projects is frequently unavailable because neither the designer nor the owner has bothered to collect the data required. A separate effort is needed to elicit this. What is desired is a sufficiently detailed breakdown of equipment cost so that the incremental cost of thermal storage can be determined.

RECOMMENDATIONS

A design procedure for thermal storage installations should be developed.

A methodology for determining the suitability of thermal storage to a particular application should be developed. This methodology should include technical as well as financial considerations and criteria.

Methodologies should be developed for optimizing thermal storage systems with respect to various parameters, such as lowest peak load, least energy consumption, least energy consumption during peak hours.

REFERENCES

1. Survey of Utility Load Management and Energy Conservation Projects, 1st Revised Report, EUS, Inc., December 1978, ORNL/Sub-77/13509/4.

2. Survey of Utility Load Management and Energy Conservation Projects, 2nd Revised Report, EUS, Inc., November 1979, ORNL/Sub-77/13509/5.

3. A Guide for Off-Peak Cooling of Buildings, Southern California Edison Company, September 1980.

Project Title: PERFORMANCE OF LABYRINTH-STRATIFIED WATER STORAGE SYSTEM FOR HEATING AND COOLING

Principal Investigator: Maurice W. Wildin

Organization: The University of New Mexico
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Project Goals: To monitor the performance of labyrinth-type stratified water storage tanks as installed in the Mechanical Engineering Building at the University of New Mexico, with a view to demonstrating the utility of this concept and to improving the performance of this type of stratified water storage.

Project Status: The project is on-going. Data have been acquired and analyzed for the 1980-81 heating season. Data acquisition and analysis are currently underway for the 1981 cooling season. Problems with maintaining the sharpness of the interface, or thermocline, between the warmer and cooler water have been encountered and analyzed. As a result, modifications of the internal partitions and passages and of the inlets and outlets have been designed. Results have been obtained for temperature distribution with modified components installed in one half of one of the tanks. The results indicate promise for improving the performance of this type of storage through maintenance of a sharper thermocline. Installation of the modifications in the other half of the one tank and in additional tanks, together with performance evaluation during both heating and cooling operation, are needed to determine the efficacy of the modifications.

Contract No.: UCC, ND Subcontract No. 7967

Contract Period: October 1, 1980 through September 30, 1981

Funding Level: $43,627

Funding Source: U.S. Department of Energy through Oak Ridge National Laboratory

PERFORMANCE OF LABYRINTH-STRATIFIED WATER STORAGE SYSTEM FOR HEATING AND COOLING

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ABSTRACT

The performance of a set of thermal storage tanks using water as the storage medium and the labyrinth technique to help maintain separation of warmer and cooler water has been monitored during most of the 1980-81 heating season and is being monitored during the 1981 cooling season. The results indicate the effectiveness of this technique for leveling of the power drawn from a utility. They also indicate the potential for energy conservation via heat recovery during the heating season. But there is a need to improve the efficiency of thermal storage for both heating and cooling if energy is to be conserved on an annual basis.

INTRODUCTION

The desirability of maintaining the design temperature difference across a thermal storage element, to obtain the design capacity of storage and to enhance the performance of equipment with which storage interacts, is apparent. In order to realize the design temperature difference requires attention to both the design of thermal storage and to control of its interactions with other equipment. In design of storage using a liquid as the storage medium, provision should be made to minimize mixing of, and heat transfer between, the warmer and cooler fluids in a tank, irrespective of the direction of flow through storage, reference 1. The storage medium of interest here is water, and several schemes for minimizing or entirely preventing mixing have been devised, reference 2. A scheme employing vertical internal partitions to help maintain separation of the warmer and cooler water and to help maximize the useful volume of each tank was developed in Japan, reference 3. Due to the relative simplicity of control and flexibility of system operation offered by this scheme, its elements were incorporated in thermal storage tanks constructed for the Mechanical Engineering Building at the University of New Mexico in Albuquerque.

TANK DESCRIPTION

The thermal storage subsystem for the Mechanical Engineering Building is comprised of eight rectangular cross-section concrete tanks, each with a nominal volume of 57 m^3 (15,000 gal) or a nominal storage capacity of 2.31×10^6 KJ (2.25×10^6 Btu), corresponding to a temperature change of 10°C (18°F). The array of tanks consists of two rows of four tanks each, arranged along an east-west axis (Fig. 1) and located at the northwest corner of the building. The tanks are at the same level as the mechanical equipment room, which is one and one-half levels below grade. However, the tops of six of the tanks serve as part of the service drive to the northwest entrance to the building, and are insulated internally with two inches of extruded polystyrene foam. The two remaining tanks at the west end of the array are buried and are insulated externally with two inches of extruded polystyrene, as are the bottoms of the other six tanks. The north walls of the four northern tanks serve as one side of the inlet air chase leading to the mechanical equipment room, and the south walls of the four southern tanks serve as one side of the exhaust air chase. Each tank is approximately cubical in configuration, being 3.6 m (11.8 ft) by 4.2 m (13.6 ft) in plan and 4.6 m (15 ft) deep. The tank walls, tops and floors are made of reinforced, poured concrete and are one foot thick. However, between adjacent pairs of tanks the north-south walls are of double thickness, with two inches of extruded polystyrene sandwiched between the concrete, to minimize heat transfer (Fig. 1). The east-west walls between pairs of tanks are not insulated, because it was conceived that the tanks would be switched from heating to cooling service in pairs. Sometimes, this has turned out to be the case; but the tanks are connected to the external pipe header system individually, in parallel; so they may be switched from cooling to heating operation individually. Access to the tanks is through manholes in the tops, for personnel, and through conduits embedded in the tops of the side walls leading to the adjacent air chases, for instrumentation cables.

The configuration of the internal partitions in the tanks is illustrated in Fig. 2. Two pairs of weirs and baffles divide each tank into three major compartments. The space between each weir-baffle pair is termed a direction change passage and, as built, is one foot wide. When charging a tank with cooling capacity, or discharging it of heating capacity, warmer water flows out of the tank through the high port on the left and into it through the low port on the right. When charging a tank with heating capacity or discharging it of cooling capacity, the flow direction is the reverse of that just stated. To trace the flow through the tank for the former case, the cooler water entering near the bottom of the right-hand compartment about 0.30 m (1 ft) above the floor displaces warmer water upward. This water spills over the weir to the left, flows down through the direction change passage, and enters the middle compartment about 0.30 m (1 ft) above the bottom through a 0.15 by 0.30 m (6 by 12 inch) port in the far end of the baffle. Thus, the direction change passage serves to conduct the fluid from the top of one compartment to the bottom of the next, or vice-versa when the direction of flow is reversed. The pattern of flow described for the right-hand compartment is repeated in the middle and left-hand compartments, and the fluid exits through the high port in the latter. This port is about 0.61 m (2 ft) below the water surface in the southern row of tanks and about 0.76 m (2-1/2 ft) below in the northern row. Each of the inlet/outlet ports is a 4-inch diameter cast iron pipe terminated with a 90 degree elbow. Thus, the incoming flow undergoes a sudden expansion and the outgoing flow a sudden contraction. Elbows were used to help impart a swirling motion to the flow in each compartment. It was felt that this would aid in minimizing unused volume, or dead space, reference 4.

The weirs and baffles are sheets of corrugated metal attached to 2 by 4 wood frames. The ends of the metal sheets protrude into grooves in the vertical tank walls, which helps anchor the weirs and baffles against lateral (east-west) motion. Elastic closure strips were attached to the ends of the metal sheets to help prevent leakage around the weirs and baffles, but this measure was not particularly effective. And, in any event, the horizontal joints between the metal sheets and between the bottom sheet and the floor were not sealed, since it was thought that little leakage would occur due to the low pressure differences anticipated between adjacent compartments. The metal sheets were not insulated to avoid additional cost and because a method for anchoring insulation securely against the buoyancy force had not been conceived. Thus the weirs and baffles, as constructed, were susceptible to both water and heat leaks. The effects of these leaks on performance are discussed later, in the section on performance of thermal storage.

OPERATION OF STORAGE WITH THE HEATING AND COOLING SYSTEM

The storage tanks serve the functions of both load management and energy conservation. The tanks are charged with both heating and cooling capacity by means of two electrically-driven reciprocating heat pump/chiller units, with a combined capacity of 580 kW (165 tons) thermal, and with excess heat collected from the sun by 289 m^2 (3108 ft^2) of solar collectors during the heating season (Fig. 3). The solar heat demanded by the load goes directly to the heating coils. Only if there is an excess does any go to storage. The tanks are discharged through the heating and cooling coils during the daytime operating period, which extends from approximately 06:00 to 18:00 in the fall, winter, and spring and from 06:00 to 20:00 in the summer. Normally, no operation occurs on weekends or holidays. Load management is accomplished by operating the heat pump/chiller units during off-peak hours, just prior to the next day's operating period, during all seasons. Thus, this operation occurs when minimum electrical power is demanded by the remainder of the equipment and lights, so it does not add either to the coincident peak of the building or to that of the electric utility. Energy conservation is achieved during the heating season by using solar energy and, via thermal storage, by recovering heat from portions of the building requiring cooling. This heat is first absorbed in the cooled portion of storage, then elevated in temperature and transferred to heated storage via the heat pump/chillers during off-peak hours. In this manner, both load management and energy conservation are accomplished in the heating season, which extends from about mid-November to mid-March, whereas only load management is accomplished in the cooling season from mid-May to mid-September. During intermediate seasons, solar energy is used exclusively for heating, and outdoor air is used as much as possible for cooling, to minimize operation of the heat pump/chillers.

MONITORING SYSTEM

A number of instruments are used, along with a computer-controlled data acquisition and reduction system, to automatically monitor the behavior and performance of thermal storage and the rest of the heating and cooling system (Fig. 4). In monitoring thermal storage, emphasis is placed on determining energy flow into and out of storage and temperature distribution in storage. To this end, temperature sensors are located in the inlet and outlet water lines to each tank and at five strategic locations in each tank (bottoms of two compartments, mid-height of all three compartments). To provide more detailed information on the temperature distribution in one tank, temperature sensors are located at one-foot vertical intervals in this tank, designated Tank No. 6. The combined water flow rates through all heated tanks in parallel and all cooled tanks in parallel are measured, so that energy flows into and out of the heated and cooled portions of storage can be evaluated separately.

Thermistors (dual thermistor probes) and thermocouples are used for temperature instrumentation. Target-type flow meters are used for most water flow rates, although one positive displacement-type meter and two vortex-type meters are used for special situations. Watt-hour meters with pulse generators are used to measure electrical energy input to major components whose power demand is unsteady, including total lighting and total building energy use. Pyranometers (precision spectral type) are used to measure solar flux on a horizontal plane and in the plane of the collectors, and an anemometer and a vane are used to measure average wind speed and direction. Other sensors include differential pressure transducers, flow switches and dew point sensors. In total, over two hundred sensors are employed.

The outputs of all sensors are sampled every 30 seconds, converted to SI units and used to calculate temperatures and fluid flow rates, thermal energy flows, electrical energy flows and weather data. At the end of each hour, a summary of data and results for that hour, including average temperatures and fluid flow rates, hourly thermal and electrical energy flows, and weather data, are recorded on magnetic tape and on paper. These data are output in a form which facilitates checking energy balances and evaluating sub-system performance. The hourly results for energy flows and for certain weather data are used to compile daily totals and monthly totals, which are also output on magnetic tape and on paper. The data recorded on magnetic tape are subsequently transferred to flexible magnetic disk for further manipulation and plotting off-line, using a separate computer.

BEHAVIOR AND PERFORMANCE OF THERMAL STORAGE

As soon as monitoring of the temperature distribution in the tanks began, it was recognized that leakage between the compartments through the weirs and baffles was occurring. During the early part of fall 1980, while the principal load of the building was cooling and the active tanks were all cooled, it was evident that cold water was leaking from the bottom of the first compartment, where it is introduced into the tank, into the bottoms of the second and third compartments. However, it was not until the results of the more detailed temperature distribution measured in Tank 6 were output in December that the effects of leaks through the weirs and baffles on the behavior of heated tanks began to become apparent. These effects may be summarized by examining Fig. 5. Figure 5 displays the instantaneous temperature distribution through Tank 6 while it was being charged with heated water from the heat pumps on January 15, 1981. Note that the order of positions on the plot is opposite that on the tank sketch inset on the graph.

Numbers on the horizontal axis correspond to linear positions along the ideal path of a fluid particle as it would pass through storage, illustrated in the inset on Fig. 5. The pairs of vertical lines represent the weir-baffle pairs. The entering water temperature was initially about 43°C, but for most of the charging period it was about 41°C (Fig. 5). Examination of the temperature distributions indicates that a temperature transition, or thermocline, thickness of about 1 m (3 ft) occurred in the inlet compartment, i.e., compartment 3. When compartment 3 is part full of warmer water, but cooler water is going through the direction change passage, the cooler water is heated as it passes through the direction change passage, as indicated by the plot for 03:45. However, when the warmer water reaches the bottom of this compartment and starts to pass through the direction change passage into the second compartment, it undergoes a significant temperature drop. This drop, initially about 5°C (9°F), steadily decreases as the second compartment fills with warmer water, but its magnitude remains significant throughout the charging phase. A similar temperature drop occurs as warmer water flows from the second to the first compartment. The result of these temperature drops, as well as an apparent mixing action in compartment 2, is that the thermocline does not pass from the third compartment into the second one, but is smeared into a mild temperature gradient. The smearing continues during discharge of the tank, with reverse flow,but this is not illustrated here.

The causes for the temperature drop and smearing of the thermocline have been investigated extensively. It has been concluded that there are three principal causes: 1) water leaks through the weirs and baffles, 2) heat flow through the weirs and baffles and 3) mixing in the compartments near the inlets. Measures were taken (repeatedly) to eliminate the water leaks through the partitions in Tank 6, until they were negated. However, the temperature changes through the direction change passages persisted. Thermocouples installed in one of these passages indicated that most of the drop occurred very near the bottom of the direction change passage. This observation appeared inconsistent with the most obvious explanation in terms of heat transfer, until it was recognized that free convection, interacting with very low-velocity forced convection could produce a convective cell within the direction change passage. The interaction might also cause an enhancement of convective heat transfer by several hundred percent, reference 5, which enhancement would explain the magnitude of the temperature change we observed in the flow through the passage.

Acting on the hypothesis that interaction of free and forced convection was occurring and that the flow through the direction change passage needed to be moved out of the mixed free and forced

BEST DOCUMENT AVAILABLE

convection regime into a regime dominated by forced convection, we designed a new direction change passage with reduced cross-sectional area, to increase the Reynolds number of the flow through it, and with increased thermal resistance in the passage wall, to reduce the Grashof number. Thermal resistance was increased both by reducing the surface area of the passage and by applying insulation to it. The resulting configuration is illustrated in Figure 6. The direction change passage is comprised of four, 10 cm (four inch) diameter PVC pipes, connected at the top and bottom through tees to headers made of the same pipe. The headers admit and discharge water through one-inch wide slots, at very low velocity. The vertical pipes are insulated with 2.5 cm (one-inch) thick, flexible "Halstead sheet" insulation, with an R-value of 2 (U.S. Engineering units).

This configuration was installed in Tank 6 in place of the old direction change passage between compartments 1 and 2, for purposes of testing. To make room for the vertical pipes, the sheet metal which comprised the old baffle wall was removed. The original weir was extended upward by about 0.3 m (1 ft), to serve as a physical barrier between the two compartments, and this wall was insulated with 2 cm (3/4 inch) thick extruded polystyrene, to reduce heat transfer between the two compartments. When these changes were completed, we had entered the cooling season, so results have been obtained only for operation as a cooled tank. The results will be presented after another pertinent change in this portion of Tank 6 has been discussed.

As mentioned previously, smearing of the thermocline is thought to be partially due to mixing near the inlets to the compartments. The sudden expansions associated with the original inlets, and the positions of these inlets relative to the tank floor, would tend to produce mixing. Since steps were being taken to improve the maintenance of the thermocline as it passed between compartments 1 and 2, it was felt desirable to try to produce a sharper thermocline near the inlet to compartment 1. Hence, a new linear inlet/outlet diffuser was designed with the objectives of introducing (or withdrawing) the water uniformly along one side of a compartment, at a low velocity. The prototype diffuser was designed to be located at the lower corner of compartment 1, opposite the barrier between compartments 1 and 2. In an effort to achieve uniform emission along the length of the diffuser, small holes 0.2 cm (5/64 inch) diameter were drilled 2.5 cm (1 inch) apart, in a length of 10 cm (4 inch) diameter PVC pipe. The hole size and spacing were selected taking into account pressure drop along the pipe due to friction, and pressure rise along the pipe due to emission of fluid from the pipe and associated deceleration of the fluid remaining in the pipe. To introduce the fluid into the tank at low velocity, the 10 cm (4 inch) pipe was mounted concentrically in a 15 cm (6 inch) pipe with a 2.5 cm (1 inch) wide slot, cut lengthwise. This slot is located about 7.6 cm (3 inches) above the floor and is oriented to direct incoming flow toward the partition between compartments 1 and 2. The slot is oriented 180 degrees from the holes in the inner pipe. Thus, the velocities of the fluid particles turn 180° as the fluid flows through the annulus between the two pipes.

The effects of the changes described above in the partition and direction change passage between compartments 1 and 2 and in the inlet to compartment 2 are illustrated in Figure 7, which presents temperature distributions in Tank 6 while it was being charged with chilled water on July 20, 1981. A relatively sharp thermocline, about 1 m (3 ft) thick was established in compartment 1. The thermocline remained relatively sharp as it moved into compartment 2, although the "tails" at the bottom and top of the thermocline grew somewhat as the thermocline move into and through this compartment. However, the thermocline smeared a great deal when it should move through the old direction change passage between compartments 2 and 3. This passage, it should be noted, has been modified from the original configuration by moving the weir and baffle together, so that the direction change passage is 8.9 cm (3.5 inch) wide, and by replacing the small port in the baffle with a slot at the bottom of it. This set of plots demonstrates clearly the improvement achieved by the new direction change passage, and illustrates the possibility of maintaining a relatively sharp thermocline throughout a daily operating cycle. However, the effects of the new configuration on the thermocline during the latter part of the charging phase and during discharging cannot be demonstrated until the partition and direction change passage between compartments 2 and 3 are modified. Hence, the effects on thermal efficiency, the "bottom line," have not been clearly demonstrated. But effort is currently being directed to obtaining results for efficiency of Tank 6 alone, for comparison with the efficiency of the entire array.

The effects of using thermal storage on power demand from the electrical utility are illustrated in Figure 8. The plot on this figure for July 23, 1981 represents a day of load-managed operation, when the heat pump/chillers were operated strictly off-peak. It may be observed that the demand is relatively flat throughout the on-peak, daytime period. The plot for June 29, 1981 represents a day when the heat pump/chillers were operated during an on-peak period, due to failure of an electrical fuse during the preceding off-peak operating period. The on-peak demand during this day was 185 kW, or 85 percent, higher than during the load-managed day. If these days represent the peak monthly demands for this bulding with and without load management, using thermal storage, it would have cost

$298 more this month to operate the building without load management, for the demand charge alone. If recently-filed time-of-day rates had been in effect, the savings on demand charge alone would have been $693.

While our results for load management, or economic savings, are encouraging, our results for energy conservation pose a challenge. In general, use of thermal storage involves energy losses from or to storage, and degradation of the thermodynamic availability of storage, although these may be compensated by using, for heating, energy that would have been wasted or, for cooling, by operating equipment under more favorable nighttime conditions. In our case, these losses are also considered to be compensated by excess solar energy, routed to storage during intermediate seasons. We decided to use a first-law definition of efficiency, namely, the ratio of thermal energy withdrawn from storage (for heating) over a period of several consecutive days, to the thermal energy supplied to storage over the same period, which avoids the question of the change in internal energy of storage since this change is very small compared to the energy flow into and out of storage. Applying this definition to a period of twelve consecutive days in February resulted in a measured thermal efficiency for heated storage of 65 percent. Our results to date for thermal efficiency of cooled storage indicate an average value of 80 percent. The latter value is higher, since less mixing and therefore less loss of availability occurs in our cooled storage than in our heated storage. Both values leave considerable room for improvement, and it is the improvements which we intend to address in the second year of our project.

CONCLUSION

A means by which inlets/outlets and internal partitions and passages may be configured to produce a relatively sharp thermocline in labyrinth-type stratified water tanks and to maintain the thermocline as it moves through the tank is thought to have been identified. However, additional work is needed to demonstrate the efficacy of these changes on the performance of thermal storage tanks.

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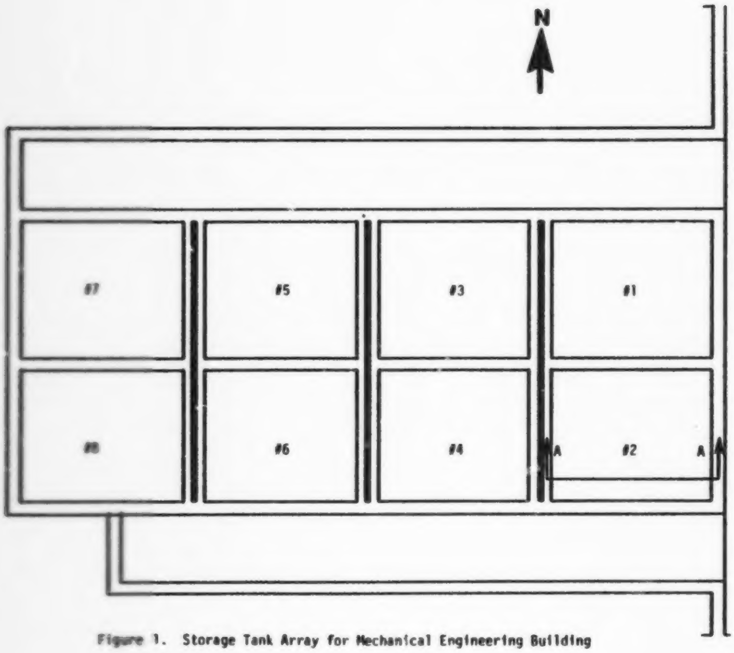
N
#7
#5
#3
#1
#8
#6
#4
#2
A
A

Figure 1. Storage Tank Array for Mechanical Engineering Building

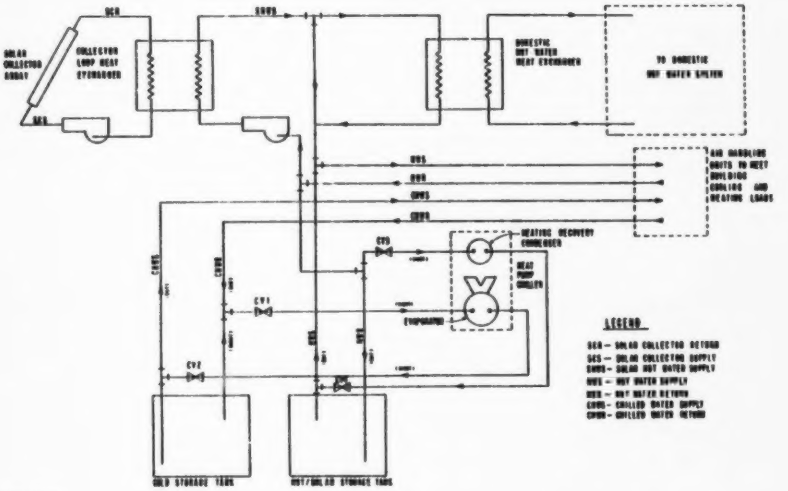
SCR
SHWS
SOLAR COLLECTOR ARRAY
COLLECTOR LOOP HEAT EXCHANGER
SCS
DOMESTIC HOT WATER HEAT EXCHANGER
TO DOMESTIC HOT WATER SYSTEM
HWS
HWR
CHWS
CHWR
AIR HANDLING UNITS TO MEET BUILDING COOLING AND HEATING LOADS
CV3
HEATING RECOVERY CONDENSER
HEAT PUMP CHILLER
CV1
EVAPORATOR
CV2
CHWS
CHWR
HWS
HWR
COLD STORAGE TANK
HOT/SOLAR STORAGE TANK
LEGEND
SCR – SOLAR COLLECTOR RETURN
SCS – SOLAR COLLECTOR SUPPLY
SHWS – SOLAR HOT WATER SUPPLY
HWS – HOT WATER SUPPLY
HWR – HOT WATER RETURN
CHWS – CHILLED WATER SUPPLY
CHWR – CHILLED WATER RETURN

Figure 3. Mechanical System Schematic, Showing Major Components

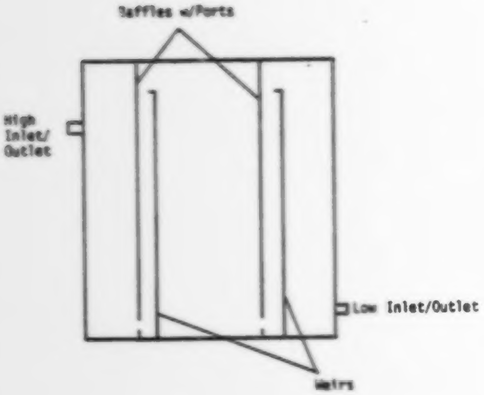
Baffles w/Ports
High Inlet/Outlet
Low Inlet/Outlet
Weirs

Figure 2. Section View of a Storage Tank with Weirs and Baffles

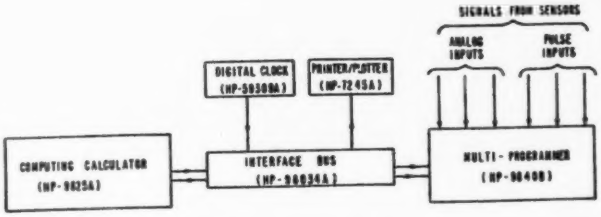
SIGNALS FROM SENSORS
ANALOG INPUTS
PULSE INPUTS
DIGITAL CLOCK (HP-59309A)
PRINTER/PLOTTER (HP-7245A)
COMPUTING CALCULATOR (HP-9825A)
INTERFACE BUS (HP-98034A)
MULTI-PROGRAMMER (HP-6940B)

Figure 4. Schematic of Data Acquisition System

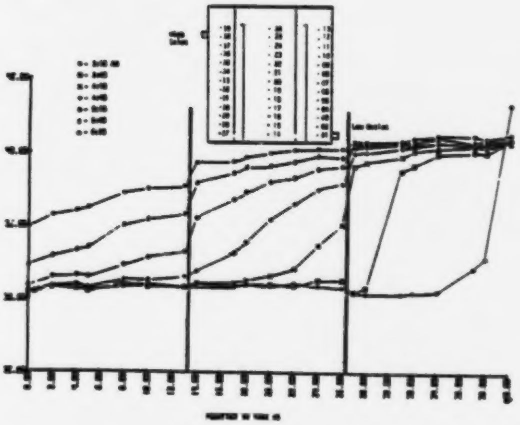

Figure 5. Temperature Distribution in Tank 6 During Charging with Heated Water, January 15, 1981

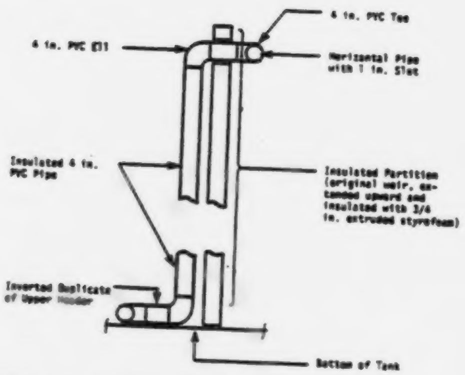
4 in. PVC Tee
4 in. PVC Ell
Horizontal Pipe with 1 in. Slot
Insulated 4 in. PVC Pipe
Insulated Partition (original weir, extended upward and insulated with 3/4 in. extruded styrofoam)
Inverted Duplicate of Upper Header
Bottom of Tank

Figure 6. Redesigned Partition and Direction Change Passage

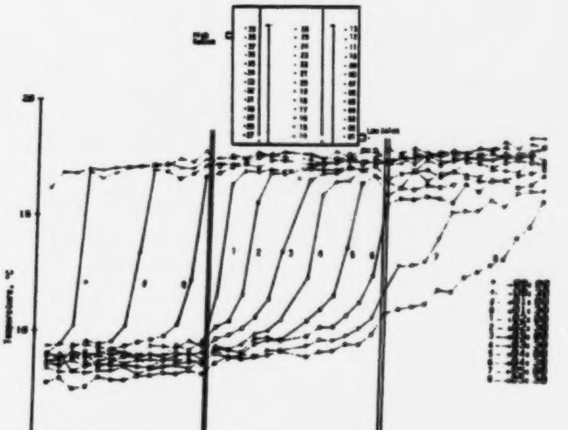

Figure 7. Temperature Distribution in Tank No. 6 During Charging with Chilled Water. July 20, 1981

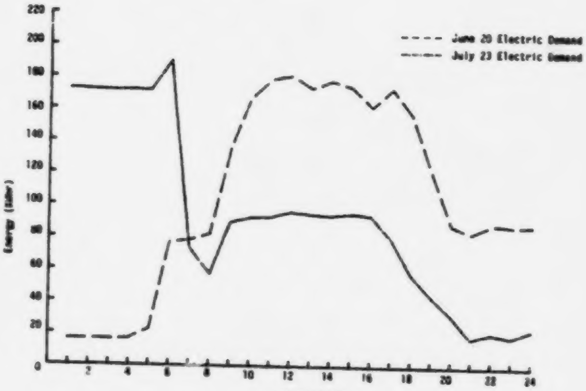

Figure 8. Hourly Electrical Energy Use for Load-Managed and Non-Load-Managed Operation

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PROJECT SUMMARY

Project Title:	Evaluation of Stratified Thermal Storage System for Oliver Springs Elementary School
Principal Investigators:	R. L. Reid and A. F. G. Bedinger
Organization:	The University of Tennessee Energy, Environment, and Resources Center 329 South Stadium Hall Knoxville, TN 37916 615-974-4251
Project Goals:	A combination of refrigeration heat recovery system and stratified thermal storage system using a flexible membrane to resist temperature blending will be evaluated. The evaluation will consist of two related parts: (1) evaluation of overall HVAC system thermal performance and comparison with alternate systems and (2) evaluation of the flexible membranes ability to resist temperature blending.
Project Status:	The stratified thermal energy storage system is expected to be fully operational by the end of August, 1981. Installation of the data acquisition system is complete with data gathering expected to begin by September, 1981.
Contract Number:	7685 (Project Authorization X60)
Contract Period:	June 1, 1980, through August 31, 1982
Funding Level:	$110,506
Funding Source:	Union Carbide Corporation Nuclear Division

PERFORMANCE OF STRATIFIED THERMAL STORAGE SYSTEM FOR OLIVER SPRINGS ELEMENTARY SCHOOL: PROGRESS REPORT

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ABSTRACT

This paper is a progress report on the performance of a stratified thermal storage system coupled with a heat recovery refrigeration machine designed to provide space heating, cooling and service water heating. Water storage tanks utilizing a flexible membrane to resist temperature blending will be used as the thermal storage element. The two design goals of the heat recovery and thermal energy storage system are (1) to minimize the need to purchase energy for space heating and cooling and water heating and (2) to minimize electrical demand. An automatic data acquisition system will be used for system performance and data gathering. Data collection is expected to begin in September, 1981.

INTRODUCTION

In many buildings, over a diurnal cycle, there is need for space heating and cooling. Moreover, there is often a need for simultaneous heating and cooling. During periods when a cooling load is being satisfied with mechanical refrigeration, the potential exists for high side heat reecovery from the refrigeration machine precluding the need to purchase additional energy for space heating. Such heat recovery systems have been successfully employed for many years when the heating and cooling loads are simultaneous. However, when space heating and space cooling loads occur during any given day (or other period) but not simultaneously, a refrigeration heat recovery system is ineffectual without a thermal energy storage system (TES). Through use of refrigeration heat recovery and TES the need to purchase heating energy can be greatly reduced potentially saving energy and money.

Another means of conserving resources and minimizing operating costs is to reduce electrical demand. The resources conserved through minimization of electrical demand consist, in most cases, of natural gas and various petroleum distillates. The dollar savings as a result of conserving these high cost, non-renewable resources can be passed on to customers assisting utilities to minimize peak demand consumption of electricity at the point of end use.

This paper is a progress report on the performance of a stratified thermal storage system coupled with a heat recovery refrigeration machine designed to provide space heating, cooling, and service water heating. The TES system is expected to be fully operational by the end of August, 1981.

DESCRIPTION OF SYSTEM

The Oliver Springs Elementary School has recently been constructed in Roane County, Tennessee. The school is approximately 68,117 square feet in conditioned floor area. The design cooling load is 1.32×10^6 BTUH and the design heating load is 1.14×10^6 BTUH. The HVAC system in the school consists of a double bundle heat recovery water chiller to enable simultaneous heating and cooling as required. There is also a natural gas fired hot water boiler for space heating when chiller heat rejection is insufficient to carry the load. Thermal storage in the form of 3 cast-in-place, concrete water storage tanks is to be utilized in conjunction with the chiller and boiler (see Figure 1). The tanks are equal in size. Each tank is approximately 3 ft^3, thus the total storage capacity is approximately 64,400 gallons of water. The tank array is insulated on the top and sides with 3 inches of urethane foam and on the bottom with 3 1/2 inches of foamglass. Each storage tank uses a flexible membrane[1] device to resist temperature blending. The flexible membrane is constructed of coated fabric and fastened to the tank walls at mid-height. The membrane can float up and down to suit variable conditions. Water level sensing wells are located in two corners of each tank with appropriate controls to sense when the membrane is at the top or bottom of the tank (see Figure 2). A screen is positioned over the sensing well outlet hole to avoid trapping the membrane against the holes.

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The two design goals of the heat recovery and TES system for the Oliver Springs School are (1) to minimize the need to purchase energy for space heating, cooling, and water heating and (2) to minimize electrical demand. During periods of the year when there is a need for space heating and cooling the HVAC system can provide such services simultaneously. Through the use of TES the HVAC system can store unwanted refrigeration system heat for later use when the demand for space heating occurs. Additionally, the HVAC system is designed such that the heat recovery chiller can operate only during un-occupied periods at times of otherwise low electrical use thus potentially saving demand charges. Through such a strategy the chiller is selected slightly smaller than the design cooling load and will operate at favorable (night) condensing temperatures for the following day thus saving operating costs, energy, and installation costs.

DATA ACQUISITION SYSTEM

An automatic data acquisition system will be used for system performance data gathering. Four types of data sensors will be used. Heat flow meters are installed in the HVAC system piping to measure heat flow from all heat sources and/or heat sinks (see Figure 1). The heat flow meters consist of positive displacement turbine meters for the measurement of fluid flow rate and solid state temperature transducers for the temperature difference measurement across the appropriate heat source or heat sink. Heat flow integration circuitry is provided with the heat flow meter and a 5 VDC square wave output proportional to heat flow is fed into the on-site data logger for accumulation. Electric power to each of the motors comprising the HVAC system (exclusive of terminal units) and total building power is being measured using solid state watt-hr transducers. The output of each watt-hr transducer is again a 5 VDC square wave signal. High and low tank fluid temperature measurements are being made using solid state temperature transducers with a milli-volt output. Weather data consisting of dew point temperature and wet bulb temperature is also being measured. An aspirated dew cell is used for the dew point temperature measurement and solid state temperature transducer for dry bulb temperature measurement.

The on-site data logger is capable of receiving the digital output from the heat flow meters and watt-hr transducers, totalizing these data, storing on magnetic tape and hard copy and resetting the counters to zero at the rate of once every half hour. Instantaneous temperature measurements will be made at the same scan interval and stored on magnetic tape and hard copy.

ANALYSIS

The overall objectives of this study are to measure the overall HVAC system thermal performance and compare the measured results with alternative systems. A mathematical model of the stratified TES system is to be developed for possible inclusion into the DOE 2.1 energy program.

Using system performance data, a heating, cooling, and water heating load profile for the school can be developed for 30 minute time steps. This data will be used as direct input into the DOE 2.1 energy program in lieu of the program making the load calculation. Thus, comparisons of energy consumption by fuel type can be made for any of the various alternative means of providing the HVAC service for the particular building. In addition, electrical demand savings will be determined for this system as compared to alternative systems.

PROJECT STATUS

The TES system is expected to be fully operational by the end of August, 1981. The automatic data acquisition system is expected to be operational by September, 1981. At the time of this writing both the TES system and the data acquisition system are installed and are being de-bugged.

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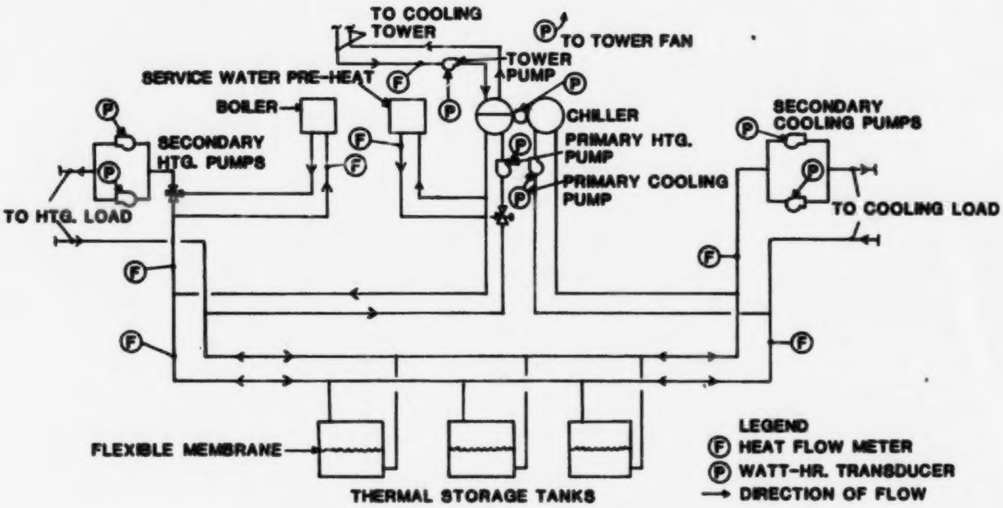
TO COOLING TOWER
TO TOWER FAN
TOWER PUMP
SERVICE WATER PRE-HEAT
BOILER
CHILLER
SECONDARY COOLING PUMPS
SECONDARY HTG. PUMPS
PRIMARY HTG. PUMP
PRIMARY COOLING PUMP
TO HTG. LOAD
TO COOLING LOAD
F
P
FLEXIBLE MEMBRANE
THERMAL STORAGE TANKS
LEGEND
F HEAT FLOW METER
P WATT-HR. TRANSDUCER
→ DIRECTION OF FLOW

FIG. 1 HVAC SYSTEM SCHEMATIC SHOWING DATA ACQUISITION SYSTEM SENSOR LOCATION

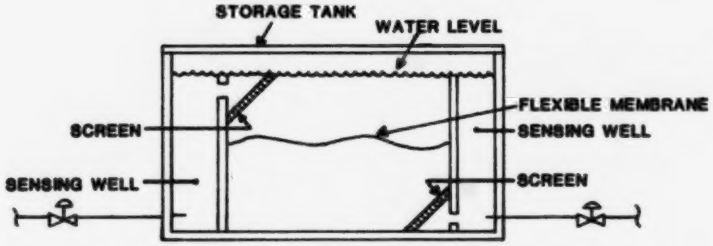
STORAGE TANK
WATER LEVEL
FLEXIBLE MEMBRANE
SCREEN
SENSING WELL
SENSING WELL
SCREEN

FIG. 2 SECTION OF THERMAL STORAGE TANK

PROJECT SUMMARY

Project Title: Development of Natural Stratification Technology

Principal Investigators: Roger L. Cole and Frank O. Bellinger

Organization:
Argonne National Laboratory
9700 So. Cass Avenue
Argonne, IL 60439 (312) 972-6230

Project Goals: The objective of this program is to measure thermal stratification and performance of vertical thermal storage tanks. The experiments to be performed on these tanks will be used to validate a semi-empirical model of stratification in vertical tanks.

Project Status: The project is approximately two-thirds completed.

A literature review has been conducted and several important concepts useful to the project have been found.

The quiescent tank experiments have been completed on the 800-gallon cylindrical tank. The natural stratification of a fully charged tank was measured, and the broadening of the thermocline in a half-charged tank was measured. Major conclusions have been made from this data.

Several discharge tests have been performed on the cylindrical tank. The measurement data is being used to validate a semi-empirical impression.

The semi-empirical model, based on one-dimensional diffusion theory, has been developed for the central region of the tank. Efforts are continuing on methods by which an empirical constant of the theory can be correlated with tank geometry.

Contract No. ACK 85379

Contract Period: March 1, 1981 through November 30, 1981

Funding Level: $110,000

Funding Source: U. S. Department of Energy through Oak Ridge National Laboratory

DEVELOPMENT OF NATURAL STRATIFICATION TECHNOLOGY

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ABSTRACT

The development of natural stratification of water in sensible heat storage tanks is studied, and comparisons of experimental data with diffusion theory equations are made. A simple 1-D model of stratification that gives good results is presented and verified with measured tank performance. A stratification index is introduced that allows a rapid comparison to be made of tank performance data. A semi-empirical equation is given that will allow a prediction to be made regarding the tank operating performance providing that an empirical constant related to the mixing heights may be evaluated. A method to estimate a value for the constant is given for the case of a tank with a side inlet and outlet. Implications of stratification in regard to overall system control strategy are discussed. The goal is to provide system designers with the guidelines necessary to assure the establishment and maintenance of stratification and to take advantage of it.

INTRODUCTION

Studies by others (1-3) have shown that thermally stratified storage can improve the performance of solar systems by as much as 20 percent compared to that of thermally mixed storage. Stratification is a function of tank design and operation and in order to assure the design of a well-stratified tank a set of tank design principles are needed. Following an acceptable tank design, an appropriate system control strategy must be adopted that will maintain the stratification and will offer the user the maximum benefits of the stratification. It is to achieve these ends that this project is addressed.

The effort includes a study of the quiescent behavior of a well-insulated tank. Here a fully-charged tank is observed in the cooling mode by use of vertical thermocouple arrays. Heat transfer takes place through the tank walls and the cooler (and therefore more dense) water flows in a thin film along the tank walls toward the bottom until a level of neutral buoyancy is attained. In this manner the tank becomes naturally stratified. A partially charged tank behaves in a similar fashion with the addition of a more pronounced broadening of the thermocline region because of thermal diffusion. The thermocline broadening in the quiescent mode is seen to follow the straightforward 1-D diffusion theory (4). Although thermal diffusion broadens the thermocline, the rate of broadening is sufficiently slow that most tanks can remain well stratified in diurnal cycling.

Tank charging and discharging tests may be performed under a variety of tank water temperatures and flow rate conditions. In order that meaningful comparisons of tank performance can be made, a stratification index that concisely summarizes the overall performance is introduced.

The basis for the prediction of tank performance is a semi-empirical expression derived from 1-D diffusion theory. The resulting expression for normalized temperature is a function of time normalized to the system time constant, the elevation in the tank, the ratio of total heat capacity to the water heat capacity, the thermal diffusion parameters, and a constant based on mixing height. When the constant can be evaluated from tank geometry, a good agreement between theory and experiment is noted. Several baffle and diffuser designs were tested in addition to the side inlet and outlet design and the conventional dip tube arrangements. For the side inlet and outlet, tank performance is seen to hold relatively constant over a wide flowrate range and then degrade markedly as a critical value for the tank Richardson number is approached. There an additional instability dominates the thermocline formation, and the dynamics involved agree with conclusions based on the Kelvin-Helmholtz instability theory.

1-D Model Equations

The quiescent mode tank behavior for a partially charged tank may be described by the expression

$$\frac{\theta - \theta_{in}}{\theta_s - \theta_{in}} = \left[\frac{1}{2} \quad 1 + \text{erf} \frac{x}{2\sqrt{\alpha t}}\right] \qquad \text{Eq. 1}$$

where α, the thermal diffusivity, is given by k/ρ cp as given by Gebhart (4). The symbols are identified in Table 1.

TABLE 1. Definition of Symbols

Symbol	Definition	Units SI	 English
θ	Tank water outlet temperature	°C	°F
θ_{in}	Inlet water temperature	°C	°F
θ_s	Tank water starting temperature	°C	°F
x	Elevation in the tank	m	ft.
t	Time	s	s
g	Acceleration due to gravity	m/s^2	ft/s^2
β	Coefficient of volume expansion	$m^3/m^3/.°C$	$ft^3/ft^3.°F$
ΔT	Temperature difference	°C	°F
L	Length of the tank	m	ft.
V	Flow velocity	m/s	ft/hr
k	Thermal conductivity of water	$w.mm/m^2.°C$	$BTU\text{-}ft/ft^2 °F$ hr
ρ	Density of water	kg/m^3	$\#ft^3$
Cp	Specific heat	kJ/Kg.°C	BTU/#.°F

The 800-gallon cylindrical tank was discharged until the center of the thermocline was approximately at the $\frac{x}{L} = 0.5$ level. Vertical thermocouple arrays in the tank were then used to measure the expansion of the thermocline as a function of time. The plot of Fig. 1 shows a comparison of the tank temperature profile as predicted by Eq. 1 (curves) and the measured values (points). Note that Eq. 1 does not include a term for heat loss from the tank and, therefore, the experimental points depart from the theory for the upper portion of the tank where a large Δ T occurs across the tank wall. However, there is good agreement between theory and experiment for the lower half of the tank where the ΔT's are small.

A fully charged well-insulatd tank was measured over a period of time to study the natural stratification. Fig. 2 shows the results of these measurements. Heat is lost from the tank through the tank walls. There, somewhat cooler water (and more dense) settles to the tank bottom to establish a temperature gradient. However, the plot shows that the main body of the tank retains a rather uniform temperature distribution.

A stratification index "S" may be defined that will allow a quantitative comparison of the various tests results. For a perfectly stratified tank the integral I = 1 where I is defined as:

$$I = \int_0^{\tau} \frac{\theta - \theta_{in}}{\theta_s - \theta_{in}} \, d\left(\frac{t}{\tau}\right)$$

With a completely mixed tank the outlet temperature decays exponentially, and therefore, the integral I for a completely mixed tank is:

$$I = 1 - e^{-1} = 0.632$$

The limits of I for a perfectly stratified and completely mixed tanks allow S to be defined such that:

$$S = \frac{I - 0.632}{0.368}$$

Values of S range from 0 for a completely mixed tank to 1 for a perfectly stratified tank.

On this basis, the data of Figs. 3 and 4 plus the results of other similar testing may be summarized as shown in Table 2. Note that S has the value of 0.85 for the discharge test of a tank with dual radial flow diffusers.

TABLE 2. Performance Summary for Several 192-Liter Tank Tests

Tank Configuration	Type of Test	ℓ/min	Stratification Index	Richardson Number
Side I/O	Discharge	7.91	0.81	3.65
"	"	14.48	0.81	1.12
"	"	23.07	0.80	0.48
"	"	30.53	0.68	0.31
"	"	34.51	0.68	0.20
"	"	46.87	0.67	0.11
Single Baffle	"	7.73	0.78	5.21
Insulated Dip Tube	"	7.71	0.77	--
Dip Tube	"	7.71	0.66	--
Concentric Baffles	"	7.73	0.61	--
Single Baffle	Interrupted Discharge	7.68	0.67	5.29
Concentric Baffles	"	7.75	0.61	--
Radial-Flow Diffusers	Discharge	7.64	0.85	225
Side I/O	"	7.99	0.75	5.47
Radial-Flow Diffusers	Interrupted Discharge	7.51	0.75	226

The last column of Table 2 gives values of the tank Richardson number (R) calculated from the expression

$$R = \frac{g\beta\Delta TL}{v^2} \qquad \text{Eq. 2}$$

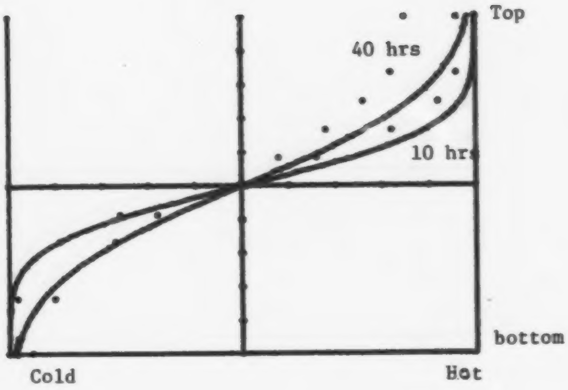

Fig. 1. Quiescent mode test of partially charged tank

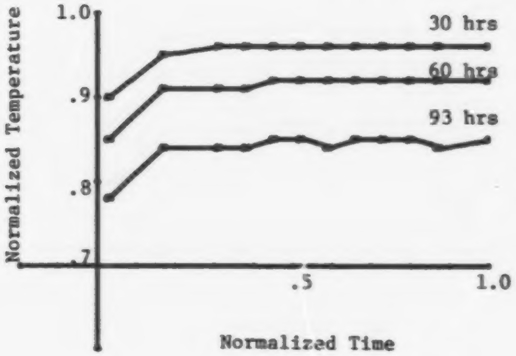

Fig. 2. Quiescent mode test of fully charged tank

Several baffle and diffuser configurations were tested for effectiveness in promoting tank stratification, and the data generated from these tests was used to develop a semi-empirical model. Figs. 3 and 4 show the results obtained from the various tests, and it is to be noted that the best tank performance was obtained using dual radial-flow diffusers.

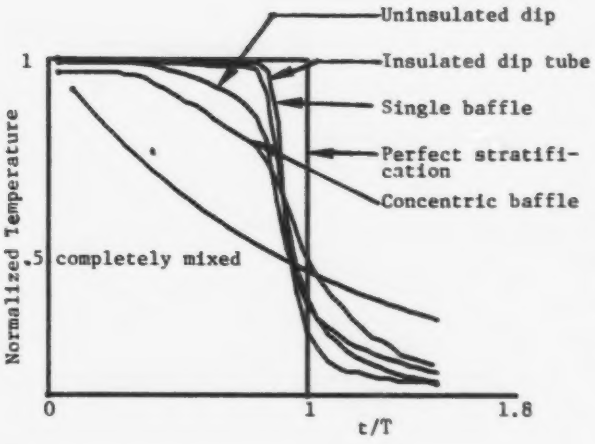

Fig. 3. Discharge test data for various tank designs.

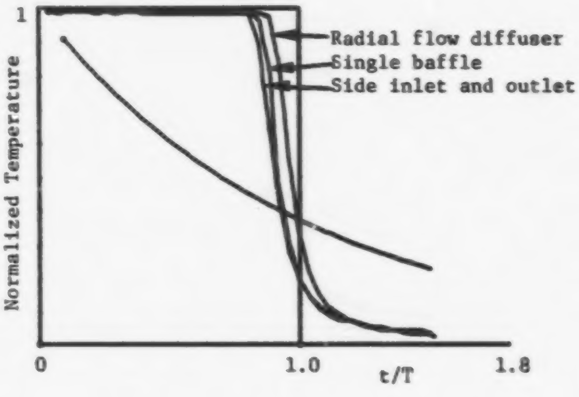

Fig. 4. Discharge test data showing improved performance of radial-flow diffuser.

The data from these tests corroborates the findings of Sliwinski, et al. (5) matches conclusions of the Kelvin-Helmholt (K-H) theory as given by Chandrasekhar (6), and demonstrates that additional tank instability from K-H interactions may be avoided provided the tank Richardson number does not approach the critical value of 0.25. Note, in particular, that for the discharge tests of a tank with side inlet and outlet, S retains a high value until the Richardson number becomes 0.31 where S then drops to 0.68. In other words, the tank may be operated with good performance over a wide range of flowrates up to the region near the critical R.

Tank performance may be predicted using the semi-empirical expression:

$$\frac{\theta - \theta_{in}}{\theta_s - \theta_{in}} = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{\frac{x}{L} - \frac{at}{\tau}}{2\sqrt{\frac{\alpha}{Lv}}\sqrt{\frac{at}{\tau}} + C}\right)\right] \qquad \text{Eq. 3}$$

where $a = \dfrac{\text{Total heat capacity of the system}}{\text{Heat capacity of the water}}$

and $\tau = \dfrac{\text{Total heat capacity}}{\text{Mass flowrate Specific heat of water}}$

The constant C used in Eq. 3 represents a modification of the conventional thermal diffusion theory to account for mixing that occurs in various regions of the tank. If C can be determined from tank geometry, diffuser or baffle design, and flow conditions, then Eq. 3 can be used to predict tank performance. Fig. 5 is a comparison of experimental data with 1-D theory of a tank with side inlet and outlet discharging at 7.99 ℓ/min. For this case inlet water was brought to the tank by a 2.86 cm (1 1/8 inch) I.D. pipe located at the side of the tank 5.72 cm (2 1/4 inch) from the tank bottom. The normalized mixing height measured to the top of the inlet pipe is:

$$\delta = \frac{5.72 \text{ cm} + 0.5\ (2.86) \text{ cm}}{157 \text{ cm.}} = 0.0454$$

and from the empirically determined relation

$$C = \left(\frac{\delta}{2\sqrt{L\frac{\alpha}{v}}}\right)^2$$

C becomes 5.8. For the outlet curve $\frac{x}{L} = 1$, C = 11.6 because two mixing zones are involved.

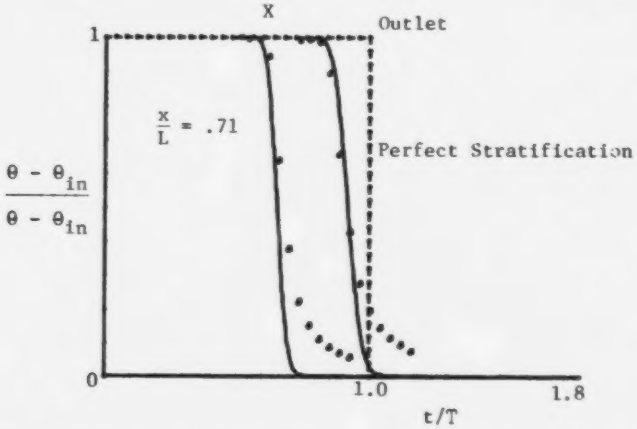

Fig. 5: Comparison of theory (curves) with experiment (points) for a discharge test of tank with side inlet and outlet.

CONCLUSIONS

1. The stratification index S described in this paper provides a means of comparing performance of two tanks or one tank under different conditions.

2. A high degree of thermal stratification in water tanks can be maintained provided that the Richardson number is greater than about 0.25 - 0.48. This is not a severe condition since it allows a wide range of useful flowrates in most solar systems.

3. Although thermal diffusion broadens the thermocline, the rate of broadening is sufficiently slow that most tanks can remain stratified in diurnal cycling. The detrimental effect of thermal diffusion can be decreased by making the tank deeper.

4. The best thermal stratification of the current set of experiments was obtained with the dual radial-flow diffuser configuration followed closely by the single horizontal baffle and the side inlet and outlet configurations.

5. Vertical baffles are detrimental to stratification because of heat transfer across the baffle. The detrimental effect was largest with the dual concentric baffle configuration which has a large area for heat transfer, but it could be clearly seen even with the insulated dip-tube configuration.

6. In the absence of vertical baffles, the temperature in any horizontal plane is approximately uniform except near the inlet and outlet. Most of the broadening of the thermocline occurs in the inlet and outlet regions of the tank. Therefore, a one-dimensional theory is sufficient in the central region of the tank.

7. A one-dimensional thermal diffusion theory that yields good results in the central region of the tank has been developed. If an empirical constant C if the theory can be correlated with tank geometry, the inlet and outlet regions of the tank can be accounted for. The theory will enable tank designers to estimate the performance of a tank before it is built and choose the most promising baffle configurations.

8. A method for determining the constant C from tank geometry for tanks having a side inlet and outlet seems to work although this conclusion is tentative at present. Preliminary data from a 3020-liter (800-gallon) tank and from flow visualization experiments do not contradict this conclusion.

9. Conventional control strategies are inappropriate for maintaining stratification. A new control strategy having the following characteristics must be used:

   1) No more than one tank volume per day can be allowed to flow through the collector or collector heat exchanger.

   2) The flow rate must be varied so that the water is returned from the collector or collector heat exchanger at a constant temperature.

   3) The temperature of the water returned from the collector heat exchanger must be reduced to the design output temperature plus a few degrees to account for thermal losses and heat exchange processes.

A conventional system typically flows about 5 tank volumes through the collector heat exchanger on a sunny day [7]. If the collector is sized to raise the temperature of storage by 30°C in a day, the maximum stratification that a conventional system can achieve is 6°C. A system operating under rule (1) can achieve the full 30°C of stratification. The necessity for rule 1 is beginning to be recognized by others [1].

A system that violates rule 2 will put water that is colder than the water at the top of the tank into the inlet. The relatively cold water tends to sink to the bottom, but since it originally came from the bottom and has been heated, the effect is to heat the tank from the bottom upward. As the temperature at the bottom increases, the Richardson number decreases. When the critical Richardson number of about 0.25 is reached, the tank mixes completely and remains mixed until long after the pump is turned off. This has been observed in monitored systems. See, for example, Figure 8 of Reference (8).

Rule 3 is made possible by rules 1 and 2. It is through rule 3 that the benefit of stratification is achieved. The reduced collector temperature allows the collector to operate more efficiently.

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PROJECT SUMMARY

Project Title: ORNL Thermal Energy Storage Program - Technical Support

Principal Investigator: Ralph N. McGill

Organization:
Oak Ridge National Laboratory
Engineering Technology Division
Oak Ridge, Tennessee 37830

Project Goals: Carry out experiments, analyses, scoping research, and assessments supporting work being done under subcontract by the Building Heating and Cooling or the Industrial Applications portions of the ORNL Thermal Energy Storage Program.

Project Status: Work progressed on three major program elements of the in-house effort during the past year.

In the area of computer modeling of phase-change behavior, more understanding of the freeze-melt moving boundary phenomenon was obtained in ORNL studies for both conduction-heat-transfer-dominated and natural convection situations. Bench-scale investigations of the freeze-melt phenomenon have supported the analytical studies. The modeling efforts were enhanced during the year through a subcontract with Kalamazoo College for corollary analytical and experimental studies of PCMs.

The liquid Thermal Energy Storage Test (TEST) Facility became fully operational under manual control during the past year. The facility is serving as a test bed for evaluating both the performance of various TES units and the newly proposed ASHRAE standards for testing thermal storage devices. A number of tests have been performed on a stratified water tank and on a PCM unit. Plans for the facility include an upgrading of its capabilities so that it can be operated in a fully automated manner.

The earth thermal storage-assisted heat pump studies have progressed to the point where well-controlled experiments are needed in order to validate both a model of the thermal performance of the earth boundary of a residential crawl space and the coupling of that same model with existing heat pump models. During the past year, the studies - primarily analyses of existing data - have bolstered, but not yet proven, the premise that the thermal inertia of the earth under a crawl space can be used to improve the efficiency of heat pumps.

Contract Number: In-house

Contract Period: Continuing

Funding Level: In-house

Funding Source: U.S. Department of Energy

ORNL THERMAL ENERGY STORAGE PROGRAM - TECHNICAL SUPPORT*

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ABSTRACT

The Technology Development portion of the Thermal Energy Storage Program is the part which is done primarily in-house at the Oak Ridge National Laboratory. The objective of this portion of the total program is to carry out experiments, analyses, scoping research, and assessments so as to complement the work that is performed on the outside under subcontract from either the Building Heating and Cooling or the Industrial Applications portions of the program. The three major elements of the Technology Development program at the present time are: (1) Computer modeling and bench-scale experiments of phase-change materials; (2) Thermal Energy Storage Test Facility; and (3) Earth thermal storage-assisted heat pump studies. This report summarizes each of these program elements with regard to their objectives and the progress of each during the past year. Also, indications of the direction that each project is taking and the progress anticipated for next year are given.

INTRODUCTION

The Technology Development group within the Oak Ridge National Laboratory (ORNL) Thermal Energy Storage (TES) Program provides technical support to the two directed components of the program - Building Heating and Cooling and Industrial Applications. Currently, in-house work comprises most of the effort of this group. This report summarizes the work accomplished during the past year by the Technology Development group.

In the following sections, each program element of the Technology Development effort will be described; progress for each during the past year will be outlined; and anticipated future results will be presented.

IN-HOUSE PROGRAM ELEMENTS

1. Computer Modeling and Bench-Scale Experiments of Phase-Change Materials:

The general objective of this effort is to develop the capability for using mathematical and physical models to predict the performance of TES subsystems and components that utilize phase-change materials. Alan Solomon of the Computer Sciences Division has aided this effort in several different areas. First, he has contributed to the understanding of a PCM undergoing change-of-phase by simple conduction heat transfer. In analyzing data from previous experiments at ORNL on melting and freezing of n-otadecane paraffin wax with an imposed constant temperature boundary condition, he found the following:

(1) that within the melted portion of the PCM, the ratio of stored sensible heat to latent heat is approximately equal to one-half of the Stefan number of the process, and

(2) that the same ratio is constant in time.

The importance of these findings to PCM devices is that as the stored latent heat of the material rises, the sensible heat must also rise proportionately to the stored latent heat. Also, this approximation, being independent of time, can be applied at any point in the melting process. This means that if one knows how much of a PCM has melted at a given time, then one can also easily know the amount of sensible heat and, thus, the total heat stored within the PCM. This analysis is reported in reference (1).

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Secondly, Solomon analyzed the data from previous wax melting experiments with natural convection included in the test set-up. His analysis showed that Nusselt numbers calculated from the experimental data are virtually the same as those quoted in the literature for turbulent free convection. The implication with regard to the moving melt front in a PCM with natural convection is that one need not use complex mathematics to describe the phenomenon. Instead, rather simple relations are found to work quite well.

In addition to the modeling work by Solomon, we subcontracted with Kalamazoo College - Dr. Ralph Deal, principal investigator - for additional analytical and experimental investigations of PCM systems. Included among the tasks to be performed under this subcontract are the development of a laser diagnostic technique for examining materials undergoing change-of-phase, the construction of a test facility for carrying out bench-scale experiments, and the development of computer models that describe the moving boundary problem in a PCM. Since Dr. Deal is submitting a written report of his work to the conference, this overview will not deal with his work in detail.

Another effort on the freeze-melt moving boundary has recently been initiated with the aid of a graduate student from the University of Tennessee. This work will build on the bench-scale experiments started a few years ago that have been the subject of much of Solomon's analyses. The initial aim with the student's work is to obtain more data from the wax melt experiments with natural convection so that more verification of existing models can be made. Eventually, this project will address more complex geometries, for example, tube heat exchangers located within the PCM.

2. Thermal Energy Storage Test Facility:

The Thermal Energy Storage Test (TEST) Facility is an in-house facility designed and built for a three-fold purpose:

1. To test and evaluate the performance of prototype residential-sized thermal storage units,
2. To test and evaluate proposed new standards and methods of rating and testing thermal storage devices,
3. To serve as a developmental test bed for future promising concepts in TES devices.

The TEST facility now consists of a liquid loop, completed and operating and depicted schematically in Fig. 1 and photographically in Fig. 2. This facility has been described previously by Mark Ternes at annual review meetings (2), (3). The reader may wish to refer to the previous reports for more details of the design of the facility. However, summarizing briefly the characteristics of the loop, it is capable of fully charging or discharging a residential-sized unit [52,800 to 528,000 KJ (50,000 to 500,000 Btu) storage capacity] within four hours. The loop can use water, ethylene glycol, or salt brine as the liquid heat transfer medium over temperature ranges of 0 to 140°C (32 to 284°F).

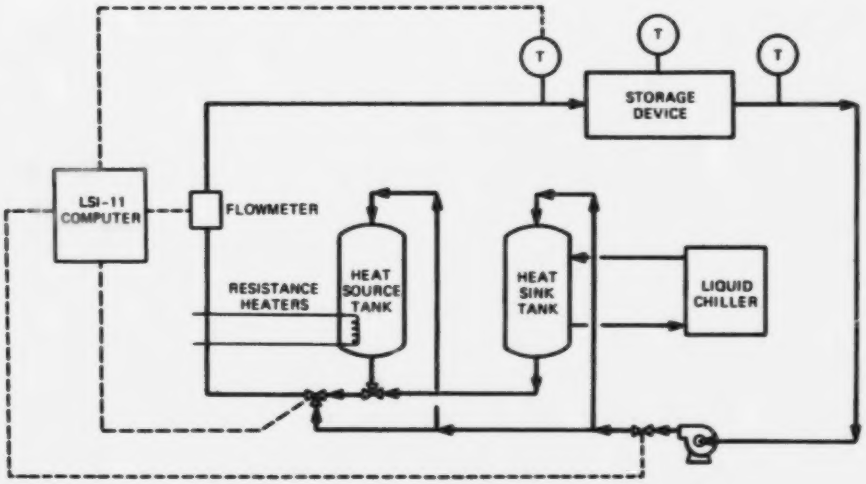

Fig. 1. Schematic diagram of test facility.

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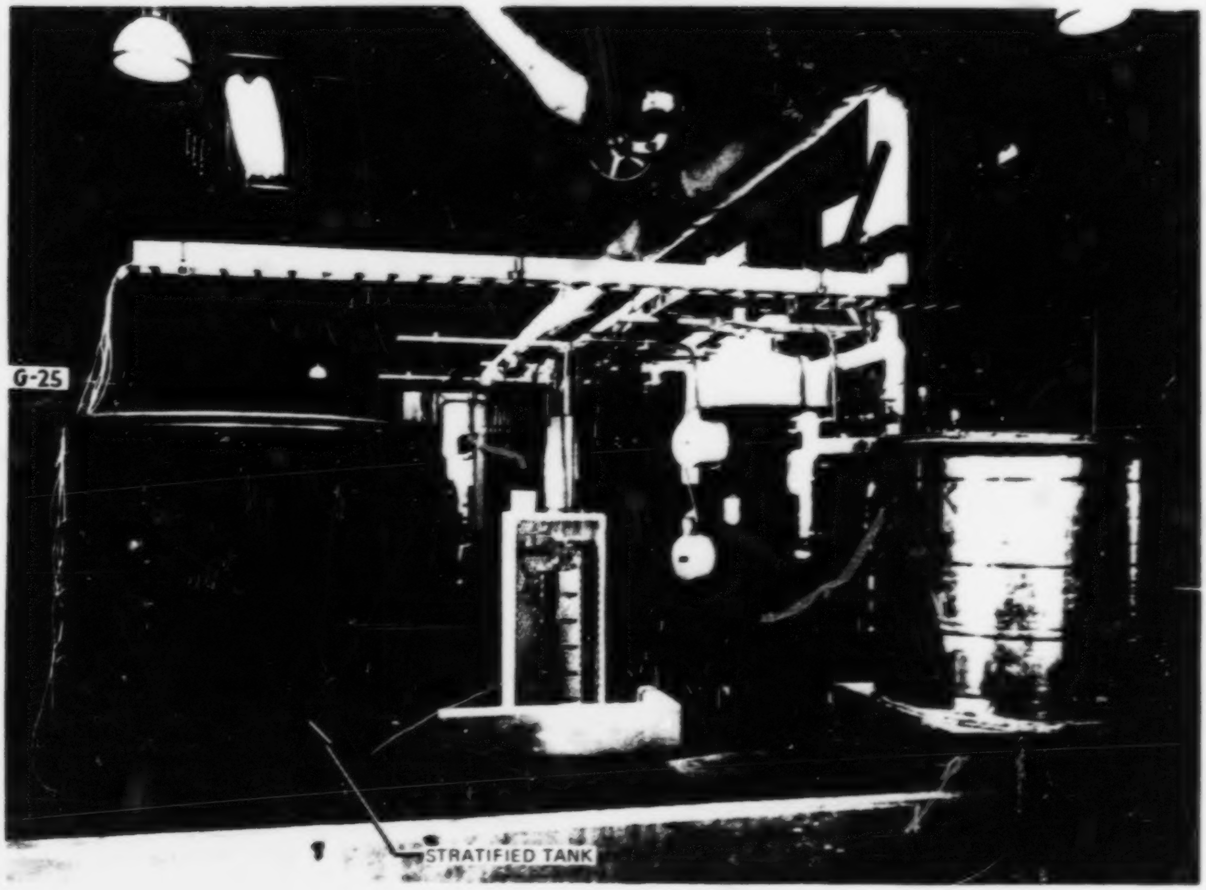

Fig. 2. Photograph of test facility.

The facility was operational under manual control early in FY 1981. Although problems have been encountered with some of the components with a resultant loss of available time for testing, considerable progress has been made. All major subsystems of the facility work well now, and only some refinement type of changes remain to be made.

We have run numerous tests of a stratified water tank as part of the testing and shakedown of the TEST facility. Although we have not embarked upon a course of developing stratified tanks, we did find some interesting results in our tests thus far. The tank, which can be seen in Fig. 2, is 1.52 m in diameter (5 ft) and 1.52 m high and holds approximately 2650 L (700 gal) of water. In our tests, we used a ΔT of 16.7°C (30°F) from 37.8 to 54.4°C (100 to 130°F). For inlet and outlet nozzles, the tank simply has radially oriented pipe fittings in the sides of the tank which can be changed in size so as to change the flow velocity of charge and discharge. Most of our tests thus far have been with inlet and outlet nozzles of 1.25 cm (0.5 in.) in diameter. With this size of inlet and outlet, we have found that good stratification behavior can be attained with flow rates of 7.6 and 11.4 L/min (2 and 3 gpm). This is illustrated in the composite graph of Fig. 3 where discharge tests of different flow rates are compared against one another and also against the ideal case. In Fig. 3 the abscissa, the time ratio, is defined as the actual time divided by the ideal time (tank capacity/flow rate), while the ordinate, the temperature ratio, is defined as the temperature difference between the temperature leaving the unit and the temperature entering the unit divided by the difference in the temperature entering the unit and the initial temperature.

In addition to charge and discharge tests of the stratified tank, we have also checked the stability of a well-established thermocline. That is, after establishing a well-defined thermocline by either a partial charge or partial discharge of a well-mixed tank, we have let the tank just sit undisturbed over a period of time to see how much the thermocline may degrade by mixing. We have found that the thermocline can remain quite stable over at least a 24-hour period.

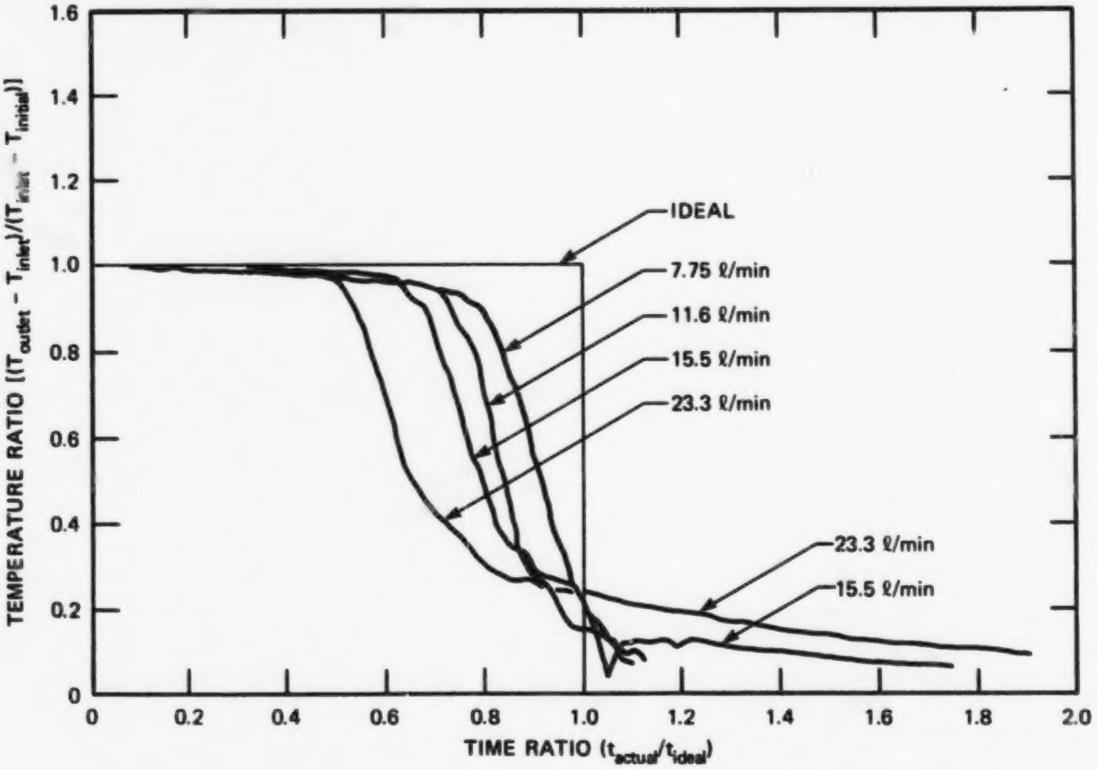

Fig. 3. Comparison of stratified tank discharge tests at different flow rates.

We have also worked with a PCM unit, specifically the Calmac HEATBANK-115 thermal storage unit. This unit, with a rated capacity of 400,900 KJ (380,000 Btu), uses sodium thiosulfate pentahydrate as its PCM which changes phase nominally at 46°C (115°F). We had initial problems with this unit with leaky fittings to the heat exchanger and a defective pump-stirrer assembly. However, after making repairs and replacements, we have run a number of tests on the unit. These tests include charge and discharge tests following the ASHRAE procedures and others. We have a two-fold objective in the work with this particular unit. One, of course, its to evaluate the unit itself as to its performance. The second is to use the unit as a test bed for evaluating proposed revisions to the ASHRAE standard procedures. With regard to both of these objectives, it would be premature to present results at this time.

With regard to improving the capabilities of the TEST facility, we have taken action that will give us the capability of automated, unattended operation. To do this, we are buying a process control software package called "PRO" from the Staff Computer Technology Corporation. This package is compatible with our LSI-11 computer and will allow us, very easily, to program automated operation of the facility. With this capability, we will be able to run longer tests, more cyclical tests, more precisely controlled tests, and weekend tests without the facility having to be manned.

With regard to the air TEST facility - the twin of the liquid facility except using air as the heat transfer medium - the following has occurred since the last review meeting: A complete conceptual design of the facility, calling out necessary equipment, specifications, and nominal sizes, was made for us by TRW under an existing subcontract. However, work has not proceeded beyond that point yet because, in our judgment, there are not enough concepts, prototypes, or products in this area yet to justify the building of such a facility.

3. Earth Thermal Storage-Assisted Heat Pump Studies:

The basic premise involved in these studies is that the thermal energy that is stored naturally in the earth under a house (specifically, a house with a crawl space) can be used to precondition the source air of an air-to-air heat pump and bring about improvements in the seasonal coefficient of performance (COP) of the heat pump. The concept requires that the outdoor air be drawn through the crawl space before being used by the heat pump, and be either preheated in the winter or precooled in the summer, by the earth which stays within a narrow temperature band year round. In the winter, for example, the preheating of the source air might bring about more efficient heat pump operation by:

1. increasing the effective capacity of the heat pump for a given outdoor temperature,

2. reducing the need for auxiliary resistance heaters, and

3. reducing the need for defrost cycles.

On the other hand, though, increased cycling losses resulting from operating at higher capacities might serve to diminish some of the three itemized potential gains above.

The progress in this study has been reported before by Mark Ternes (4), (5). The most recent report, including the most recent results, was presented by this author in reference (6). The interested reader is urged to consult the three cited references for details of the experiments performed and results to date.

To summarize briefly the conclusions reached in these studies thus far, we have found the following:

1. Substantial preheating of the heat pump source air can be accomplished by using the thermal energy stored in the earth under a residential crawl space. The preheating effect can amount to as much as 11 to 14°C (20 to 25°F) when the outdoor air temperature is about -15°C (5°F) and tapers off to virtually no gain when the outdoor temperature is about 13°C (55°F).

2. A separate experiment designed to isolate, as much as possible, all heat sources other than the earth confirmed the premise that the heat comes from the earth.

3. The preheating effect by the earth can be sustained for an entire heating season in the Oak Ridge area.

4. An analysis of data from the crawl space air and from different depths within the earth showed that heat transfer, by simple conduction from the upper 0.3 m (1 ft) of earth, can account for all the heat gained by the air.

At the same time that experiments have been proceeding, analytical modeling work - again by Alan Solomon - has progressed to the point where validation of models is necessary. Solomon has previously developed a two dimensional time-dependent model of the heat transfer and thermal performance of the earth underneath a crawl space. With this model, for given outdoor temperatures and given flow rates of heat pump source air through the crawl space, one should be able to predict both the transient thermal performance of the earth and also the preheating of the air. However, numerous assumptions, heat transfer coefficients, etc. in this model need to be validated before the model can become predictive. Secondly, Solomon can couple the earth heat transfer model with existing heat pump models to try to predict the effects of the earth thermal storage on the peformance of the heat pump. Again, though, the models must be validated with experimental data before they can be useful.

Therefore, the thrust of these studies during the coming year will be to do the experiments necessary to validate both the earth heat transfer model and the heat pump model. Having done this successfully, we will then be able to predict the extent of the benefits that may be attained by using this concept of earth thermal storage-assisted heat pump in various parts of the country.

SUMMARY

This paper has reviewed the status of the three major elements of the Technology Development portion of the TES program. The modeling of the freeze-melt process of phase-change materials has made considerable progress this year especially with the inclusion of the phenomenon of natural convection as part of the model. This program element should progress even more in the coming year because of increased attention being given to the effort both in-house and with a subcontract with Kalamazoo College.

The liquid Thermal Energy Storage Test facility reached maturity this year and is operating nearly full time now. With the facility we have learned of some interesting aspects of a stratified water tank and a PCM unit. The facility is also being used to assess proposals and to develop our own proposal for a new procedure to replace the existing ASHRAE 94-77 standard for testing thermal storage devices. In the near future the facility will be upgraded in capability so that computer controlled, automated operation will be possible.

The earth thermal storage project has moved this year to the point where we need very definitive experiments to validate computer models that have already been developed. These experiments, which are planned for the coming year, will also give us some very definite results with regard to the benefits that may be attained by using the thermal energy stored naturally in the earth to aid a residential heat pump.

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PROJECT SUMMARY

Project Title: Mathematical Modeling of TES Subsystems

Principal Investigator: A. D. Solomon

Organization:
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Telephone: (615) 574-8696

Project Goals: To develop mathematical techniques for predicting the performance of TES subsystems based on PCM's. Parallel to this, to perform simulations relevant to projects of current interest.

Project Status: A number of computer simulation programs have been prepared, of varying flexibility and applicability. In last year's report we mentioned the TES program, the array simulation program used in air conditioning assist and the pure conduction earth model. During the past year continued strengthening of these programs has taken place. This includes the development and debugging of a multilayer version of TES, extension of TES to include radiation (fourth power) boundary conditions and the incorporation of heat source terms. In this year closed form, easily computable expressions have been obtained for the behavior of an array of PCM cylinders in the crossflow of a heat transfer fluid. Simple models were obtained incorporating natural convection in the melt and were verified via wax melting experimental data. A model was developed for the "mushy zone" in freezing wax, based on earlier data in the literature. Work continued on the concept of the crawl-space heat pump. An interpretation of the Stefan number was found, and some interesting properties of melting and solidification processes were discovered for some basic melting and solidification processes.

MATHEMATICAL MODELING OF TES SUBSYSTEMS

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Nuclear Division
Oak Ridge, Tennessee

ABSTRACT

We describe results of research into phase change models for latent heat storage. These are of both a simulation and analytical nature and continue the work of past years in this effort.

INTRODUCTION

We describe some results of latent heat storage subsystem modeling obtained during the past year. These include 1) a simulation code for the cooling and dehumidification of an air stream due to PCM cylinders; 2) approximate relations for the behavior of a PCM cylinder array; 3) the development of a "bogus" specific heat for phase change calculation; 4) a simple natural convection result; 5) an interpretation of the Stefan number for a phase change process; 6) the possible incorrectness of standard approximation techniques for large Biot number; and 7) determination of earth thermal conductivity from crawl space heat pump data.

BACKGROUND

Our context is a model of a phase change process. In addition to standard notation (T = temperature, K = conductivity, c = specific heat, ρ = density, $\alpha = K/c\rho$, h = heat transfer coefficient), we will use ΔT = system temperature drop, H = phase change latent heat, St = Stefan number = $c\Delta T/H$, Bi = Biot number = hL/K for L a "typical" system length.

AIR CONDITIONING ASSIST CODE

A program has been written [1] simulating the thermal storage process in an array of PCM cylinders placed in a duct through which a heat transfer fluid (air) is flowing. The program permits time dependent changes of air flow, humidity and temperature at the duct inlet and predicts the temperature of the chubs, dehumidification (when it occurs) and outlet air characteristics. The program has been run for a substantial number of scenarios and has been tested for correct energy balances, stability and consistency.

APPROXIMATE RELATIONS FOR A PCM CYLINDER ARRAY [3]

As an outgrowth of the above, simple hand-calculator relations were derived for an array of PCM cylinders in an air flow through a duct. The relations were compared with the results of many computer simulations, and were found to give predictions accurate to within a 10% relative error. Typical results are shown in Table I for the duct outlet air temperature over a 19 hour period.

TABLE I. OUTLET AIR COMPARISON [3]

time (hr)	Outlet Air Temperature (°C)	
	Computed	Approximation
1	12.76	12.76
3	12.76	12.76
5	12.74	12.75
7	12.71	12.72
9	12.64	12.68
11	12.52	12.56
13	12.28	12.42
15	11.86	12.17
17	11.07	11.44
19	9.67	10.47
21	7.33	7.84
23	4.59	4.44

A "BOGUS" SPECIFIC HEAT

The computer simulation of heat transfer processes without phase change is much simpler and better understood than with phase change. This is particularly so when we wish to employ existing heat transfer codes for buildings and other structures. Is it possible for us to find a "bogus" specific heat for the pure conduction problem whose effect will be to mirror the process occurring with a phase change? We have shown this to be the case for the simplest classical Stefan problem. For simulating an interior PCM-filled wall we have obtained such a "bogus" specific heat under a solar flux with heat interchange between the wall and a room. Further work on this problem is continuing.

A NATURAL CONVECTION RESULT

Ralph Deal has performed wax-melting experiments at ORNL in which natural convection appeared to be the dominant heat transfer mode in the melt. By straightforward analysis we have verified that the data is consistent with the process of turbulent free convection in the melt. Indeed for many cases this result shows that when free conduction is dominant in the melt, the heat transfer analysis is direct and very much simpler than when conduction is dominant.

AN INTERPRETATION OF St [2]

For a simple melting process we have shown that the ratio of the sensible heat to the latent heat stored is independent of time and given approximately by St/2. Among other implications of this result is the fact that the sensible heat stored can be estimated from a single observation of the melt front location and that the system temperature drop ΔT cannot be made arbitrarily small for a given rate of latent heat storage.

APPROXIMATIONS FOR LARGE Bi [6]

When Bi is too large the Goodman and Megerlin methods should not be applied to a phase change process with a convective boundary condition. Indeed, we have seen that the resulting predicted process will be physically unattainable and lead to impossibly optimistic heat storage and release rates.

EARTH THERMAL CONDUCTIVITY

In buttressing the assumption that pure conduction was the dominant heat transfer mode in the earth for data reported upon last year [8], this data was used to predict the ground thermal conductivity via standard heat balances. We obtained a value of the conductivity agreeing with textbook values of K for earth. Thus there is no basis for assuming more exotic heat transfer scenarios at this time.

OTHER RESULTS [4,5,7,8]

Using various tools of analysis we have obtained additional approximations and bounds for a variety of phase change processes. These include new lower bounds on energy stored and long term behavior of the front under various conditions.

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TES FOR INDUSTRIAL APPLICATIONS

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PROJECT SUMMARY

Project Title Application of Thermal Energy Storage to Process Heat Recovery, Phase III, Heat Exchanger Evaluation

Principal Investigator: L. B. Katter

Organization: Rocket Research Company
11441 Willows Road
Redmond, Washington 98052

Project Goals: The overall goals of the Phase III Heat Exchanger Evaluation are to develop data which will enable the design of a heat exchanger suitable for long-term continuous operation in the aluminum plant pollution control system environment and to assure that the installation of such a device will have no negative impact upon the existing processes.

Project Status: The project is beginning the third phase of a four-phase program. First phase, Preliminary Investigation, and second phase, Technical and economic analyses, have been completed. Final printed reports for the second phase are in preparation.

A series of tests starting with small-scale experiments and expanding in magnitude to a production prototype is currently in process. The smallest scale testing is complete. Information gathered has been used to define a subscale heat exchanger. The subscale heat exchanger is currently being fabricated. Preparations for its installation are underway currently.

Contract Number: 86 X-61624C

Contract Period: February 1, 1980 - May 31, 1984

Funding Level: $900,000 (Fiscal Year 1981)

Funding Source: U.S. Department of Energy through Oak Ridge National Laboratories

APPLICATION OF THERMAL ENERGY STORAGE TO PROCESS HEAT RECOVERY, PHASE III, HEAT EXCHANGER EVALUATION

L. B. Katter
Rocket Research Company
Redmond, Washington

Under a Department of Energy contract, Rocket Research Company, a division of ROCKCOR, Inc., and Trans Energy Systems, Inc., a subsidiary of ROCKCOR, Inc., are investigating the use of thermal energy storage to improve the utilization of reject process heat as a source of energy for a district heating system. The specific energy source being studied is the aluminum reduction process. The energy supply in an aluminum plant is continuous and constant, 24 hours per day, 365 days per year. The energy demand in a district heating system is highly cyclical, on a diurnal basis, an annual basis, and a third cyclical variation in demand is found in the weekly use patterns. Thermal energy storage improves the cost-effectiveness of investments in energy recovery and distribution equipment and decreases the need for supplemental fuel for the district heating system.

During earlier project phases, the requirements for such a system were defined technically and economically, and problem areas identified. The experimental research under way at the aluminum plant to investigate these problem areas is the subject of this paper.

Constituents of the gas have been identified which could corrode and foul a heat exchanger used to extract energy from the gas stream. The test program will lead to a determination of the effects of corrosion and fouling on the design and operation of the heat recovery system, and means to mitigate these effects will be investigated. In addition, effects of the operation of the heat recovery system on the aluminum reduction plant process will be measured. The overall goal of the Phase III Heat Exchanger Evaluation is to develop data which will enable the design of a heat exchanger suitable for continuous operation in the severe aluminum plant environment. A series of tests has been conceived to accomplish this goal in a cost-effective manner. These tests are escalated gradually in scale in order to provide a maximum of information with minimum test investment.

First in the series were preliminary investigations including (1) gas and solid sample collection and analysis from an aluminum reduction plant, (2) a corrosion test series, and (3) small probe heat exchanger component testing. The gas analyses were undertaken to attempt to isolate and identify potential corrosive species in the gas. In the longer term it will be possible to determine the effects of the heat exchanger installation on the plant process by comparing analyses before and after the heat exchanger is in operation.

A number of tests were done on deposits obtained from the air pollution control ducts. These deposits are expected to be similar to the fouling on the heat exchanger surfaces. The purpose was to identify the constituents of the solids accumulation in order to determine the mechanism by which the solids accumulate on surfaces and obstructions in the duct. The component of the dust which causes the scaling is under investigation. Possibilities include mechanisms involving carbon, sulfur, or moisture.

The corrosion tests were directed toward the selection of an appropriate construction material for the heat exchanger. The testing consisted of two components--the examination of coupons removed from existing ducts, and an ASTM corrosion test. The examination of coupons will provide data on the exposure of mild steel to the gas environment over the life of the existing ductwork. Since the heat exchanger must be designed for a 30-year life, an accelerated stress corrosion test was begun to project the behavior of various materials over required design life.

A set of tests involving small probes was undertaken to investigate the fouling phenomenon directly. Small probes were made from representative samples of heat exchanger tubing and inserted in the ductwork in locations chosen to represent the range of conditions to be expected in the heat exchanger. Observations of the fouling accumulations were made and measurements of the heat transfer rate on clean and fouled tubes were taken.

The results of these preliminary tests indicate that a baseline heat exchanger design using finned tubes and carbon steel heat transfer surfaces is appropriate, both from the standpoint of fouling accumulation and corrosion.

The next step in this graduated series of tests is the fabrication and installation of a subscale heat exchanger. Conducting a reduced scale experiment permits valuable data to be gathered with a relatively small investment. It will be important to design a subscale heat exchanger which will provide a maximum of useful data under conditions which will permit the design to be accurately scaled up. It must be operated throughout the year to gather data during all portions of the weather and load cycles.

TEST HARDWARE DESCRIPTION

In order to satisfy the objectives of the subscale heat exchanger test as outlined above, it is imperative to gain experience with a heat exchanger installation under operating conditions. Intalco Aluminum Corporation has agreed to allow access to their facility in Ferndale, Washington, for the purpose of conducting the research outlined above. The test facility will consist of a reduced scale system. The system will extract heat from the effluent gas stream from 5 of the 720 pots at the Intalco reduction plant.

Characteristics of the baseline prototype heat exchanger design as presently envisioned are given in Table 1. The inlet and outlet gas temperatures are selected to be consistent with the gas stream temperatures and the requirements of an effective heat exchanger design. The fluid streams are arranged in multipass crossflow closely simulating true counter-flow in order to maximize heat exchanger effectiveness. Gas will flow vertically downward, making use of buoyant forces as well as providing a mechanism for collecting the dust which will accumulate on the tubes. A hopper will be provided at the bottom of the heat exchanger, equipped to collect and remove the dust. Results of the corrosion and gas environment research indicate that the preliminary tube material selection of carbon steel is appropriate. The results of the probe testing program indicate that there will not be a severe fouling problem at operating conditions. Finned tubes can therefore be used resulting in a smaller, lighter and less costly heat exchanger than would be possible with bare tubes. The fin dimensions of 3/4" high by .05" thick, with a pitch of 3 fins per inch, are recommendations of optimum design by manufacturers that have been consulted. Probe tests have been conducted with samples of finned tubing with those dimensions and have not exhibited a severe fouling problem.

Table 1

Baseline Prototype Heat Exchanger
Design/Performance Summary Table

1. Flow Arrangement — Multipass Cross Flow/Counter Current

2. Flow Conditions:	Tube	Shell
Fluid	Water	Gas
Inlet temperature, °F	135	255
Outlet temperature, °F	210	163
Flow rate, lbs/hr	166,760	578,000
Fouling factor	0.001	0.01

3. Heat Exchanger Design:

Flow area : L = 19.0 ft, W = 7.36 ft
Number of tubes, wide : 22
Number of tubes, deep : 26
Tube length : 19.0 ft
Tube pattern : Square, tubes on 4" centers
Fin O.D. : 3.375 inches
Tube O.D. : 1.8750 inches
Tube wall thickness : 0.1370 inch
Tube header size : 6.0 inch pipe size (I.P.S.)
Fins/inch : 3/inch
Fin height : 0.75 inch
Fin thickness : 0.050 inch
Fin and tube material : Carbon Steel
Tube side velocity : 2.54 ft/sec
Shell side velocity : 41.85 ft/sec
External surface area : 34,169.0 ft^2
Log mean temperature differential : 35.83°F
Heat transfer rate : 8.333 Btu/hr-ft^2-°F
Heat transfer : 10,200,000 Btu/hr
Tube side pressure drop : 4.27 psi
Shell side pressure drop : 3.08 inches H_2O
Shell side pressure drop : 3.76 inches H_2O
(Including the entrance and exit effects)

The necessary reduction to subscale size can most conveniently be made by taking a streamwise slice of the baseline heat exchanger design which results in a heat exchanger with the same flow velocity and path lengths as the baseline prototype device in a reduced number of parallel water streams. The test hardware is designed to minimize the effects of the reduction in scale from the baseline design. Fluid flow rates were reduced proportionately. The heat exchanger shell area will be relatively large in the reduced scale experiment, so the shell will be insulated to reduce heat loss to the surroundings. The shell walls will be configured to simulate an adjacent bank of tubes to accurately model the gas-side pressure drop. With these precautions, scale-up of the test data should be straightforward.

There are two conflicting requirements which affect the sizing of the subscale heat exchanger. In one direction, it should be large enough to avoid variations in gas temperature caused by the opening of hoods on individual pots which occurs as part of Intalco's normal operating procedure. In order to add raw material to the pots, the operator normally opens the hoods on two adjacent pots simultaneously. The hoods remain open long enough to enable the operator to agitate the surface and add alumina to each of the two pots in turn. Previous studies by RRC indicate that a heat exchanger large enough to include the gas stream from seven pots would be required to maintain steady-state conditions within 5 percent. If the operating procedures are revised to require the opening of only one pothood at a time, the heat exchanger may be reduced in size to include the gas stream from only five pots while maintaining steady-state conditions within 5 percent.

In the other direction, the system should not be large enough to make it difficult to dissipate the energy collected during the subscale heat exchanger test program. Due to the high cost of the hot water transmission piping from the Intalco plant to Bellingham, it is not feasible to use a district heating system as a load. It has therefore been necessary to identify a load at or near the Intalco plant. It would be preferable to connect as large a useful load as possible, using a dummy load for whatever portion is not available. The heat exchanger output should be chosen to match the local load, within the constraints of steady-state operation described above.

Space and domestic hot water heating at the north changehouse at Intalco's Ferndale plant has been identified as a load that matches the 850,000 Btu/hr available from the test system. A control system has been designed to make best use of the heat to satisfy the highly variable hot water and space heating loads, while maintaining the steady-state heat exchanger conditions required by the experiments. The energy from the heat exchanger test system will offset 96 percent of the natural gas presently used for space and water heating at this location. The useful application of the energy available from this experiment represents an annual savings of $24,500 at present prices, and will compensate Intalco to some degree for allowing installation of this experimental facility in their plant. Heat available from the test system in excess of demand will be dissipated via the normal process water outfall. This will have a negligible effect on the average outfall temperature (approximately 0.3°F).

PROJECT SUMMARY

Project Title: Bellingham Phase III, Engineering and Technology Development for a Hot Water District Heating System Employing Thermal Energy Storage

Principal Investigator: Gerard L. Vanroyen

Organization:
Trans Energy Systems, Inc.
14711 N.E. 29th Place, #101
Bellevue, Washington 98007

Project Goals: Develop thermal energy storage concepts for generic district heating schemes.

Develop computer software to: model district heating systems applications, approximate network component sizing, and determine their economic feasibility.

Develop financing mechanisms for district heating systems.

Project Status: Preliminary surveys of the users have been made to determine approximate size of equipment and heat consumption rates. Schematics have been developed with various:

Storage size and location.
Topping size and location.
User equipment size and type.

Computer software has been developed to size and evaluate storage and topping in a system.

Financing problems examined and include:

Formation of a municipal utility district to issue bonds and supervise the DHW system.

Contracts with the waste heat supplier.

Computer economic analysis of payback and capital investment commercial and residential.

User contracts with the public utility.

Contract Number: Sub Contract 86X-61622C

Contract Period: December 1, 1980, through May 31, 1984

Funding Level:
Total Project $3,516,466
Current through September 30, 1981 $175,000

Funding Source: U.S. Department of Energy through Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratories

BELLINGHAM PHASE III

Engineering and Technology Development for a Hot Water District Heating System Employing Thermal Energy Storage

Gerard L. Vanroyen Jake E. Collins Mary A. McGee
Trans Energy Systems, Inc.
Bellevue, Washington

ABSTRACT

Evaluation of thermal energy storage in a district heating system requires the integration of customer consumption rates, weather and other system operating conditions, as well as economic payback. Generic methods of approaching and evaluating these factors are essential to insure the most economical district heating projects are selected for development and that those systems are designed and operated in the most cost-efficient manner. Also, governmental and legal guidelines for interfacing with users, financing, and municipal utility regulations have been examined.

INTRODUCTION

Prior to the 1970's energy crunch, evaluation of heating and hot water systems for buildings consisted of sizing for peak demand and providing individual heat sources to meet that demand. Even within the same building, independent sources consisting of gas, electricity and oil were commonly used to provide space heating hot water and process heat. System sizing and economics consisted of the peak demand and degree day estimation which routinely ran 20-30 percent over actual annual consumption.

Demand analysis in a community, versus an independent system, shifts from peak demand to diversified usage. The larger the number of independent users the greater the sizing problem. When using a finite heat source, storage and/or topping must be evaluated for peak usage, but system economics must be evaluated in terms of optimum combinations of storage, fossil fuel topping, and reclaimed heat systems. Peak demand and usage must be tied to hourly availability of the recoverable heat source. Weather data and other data needs to be realistic in cumulative community usage to avoid gross over sizing of the system.

Location and capacity of storage and topping in the district heating network has a marked effect on size and cost of individual components, as well as overall distribution system size, power consumption and control.

Approaching the actual setup of a district heating system in Bellingham, Washington, legal, financial and administrative obstacles had to be overcome. Contracts were developed for residential, municipal, and commercial users of the district hot water to handle billing administration, and a municipal utility district had to be established. Legislation on the State level was required to allow formation of this body. Contracts to supply the waste heat with local industry had to be created, and availability of a steady source of reclaimed energy had to be guaranteed to insure payback of the system capital expenditures.

These steps are all necessary before financing and favorable bond markets can be explored.

PROJECT GOALS

Development of Thermal Energy Storage and Generic District Heating Concepts

Using Bellingham as a typical example of a district hot water system, Trans Energy Systems is developing generic configurations for: storage, distribution, user interface and topping system.

Storage concepts to be evaluated and designed include stratified storage tanks, distributed versus central storage, economic evaluation of relative costs, and establishing effectiveness of these storage methods. Storage problems, such as heat loss, flow rates, expansion, and pressure will be examined and solutions and schematics to handle these parameters will be developed.

Work currently in progress is directed towards studying the effects of thermal storage on different types of operating concepts. Fluctuating and steady-state heat sources are being coupled to various types of heat loads. Thermal storage accompanied with peak heating facilities are being analyzed at the heat source end, the user end, and at localized substations. The goal of this study is to establish the optimum system configuration for appointed heat sources and heat users, and to define how thermal storage can be used to improve the service of heat from supply to demand.

Computer Software Application Goals for Storage and District Hot Water System Evaluation

Long term goals involve completion of three major generic computer analyses:

1. A preliminary program to provide a first approximation of the district hot water heating system. This will be a simple program to quickly evaluate heat source, network costs, and users to screen potential projects for economic feasibility.
2. An engineering aid program which models the actual system. It will include pipe sizing, storage placement, topping usage, load determination, system fine tuning, optimizing equipment and operating conditions.
3. A utility aid program to simulate system operation so that the utility can add customers, predict usage and manage the district heating system most efficiently.

Developing Financing Techniques for District Heating Systems

The following goals for this phase of the project have been established:

1. Prepare necessary contracts to secure financing repayment, e.g., contracts between system owner/operator and energy suppliers and energy consumers.
2. Identify possible public and private financing mechanism and combination of mechanism for financing the baseline district heating system.
3. Compare financing expense complexity and availability of revenue (i.e., general obligation bonds, revenue bonds, traditional private financing, and leverage leasing for baseline system).
4. Identify potential for use of Industrial Development Bonds in financing the baseline system.
5. Identify possible constraints to cornering public and private finance mechanisms, e.g., restrictions on Industrial Development Bonds, public financing of private interests, and limitations on general obligation bonds.
6. Identify tax advantages for private financing, e.g., investment tax credit and energy tax credit.

PROJECT STATUS

The Bellingham Field Test System

Heating program investigations were started by selecting a group of heat users that could later be served by the Intalco Aluminum Plant heat source. The site was chosen in close proximity to a temporary heat source and was chosen to typify a representative variety of the users that Intalco would supply. The total design heat load of the system is $18(10)^6$ BTU/hr or 5.3 MW.

Development of Computer Software to Handle District Heating System and Storage Optimization Analysis

In order to utilize the maximum amount of the district hot water system heat source and economically trade off capital costs of the distribution network, Trans Energy Systems developed a series of programs to analyze the system under actual operating conditions. The following generic programs were assembled:

REDUXI is the preliminary data reduction program for an hourly and monthly system of evaluation. REDUXI is currently set up to reduce cumulative data into mean, max and min points on an hourly and monthly basis. This program was written to allow use of existing weather service data. For example, 17 years at Bellingham, or 158,000 pieces of data, is reduced to 3 files of 288 pieces of data. As specifically applied to the Bellingham project, the worst recorded weather conditions can be evaluated for a given month by the hour for peak demand sizing, hourly demand for sizing and economic evaluation, and minimum monthly/hourly demand to calculate minimum demand during possible low usage years. Maximum and minimum possible demands establish design parameters for flow and controls.

REDUXX scans the data and picks out individual days and years. This is important because it provides the ability to simulate actual weather conditions.

HWUSE is the basic program to calculate domestic hot water demand by the hour. The program currently reads from a data file which is an hourly demand curve for hot water. The calculations for hot water use and these files are currently based on ASHRAE curves; the demand curve is modified for occupancy, type of building (residence, etc.), size of storage tank, and heat exchanger.

COMHWUSE (hybrid of HWUSE) analyzes hot water consumption for schools, food services, commercial businesses, and homes. It calculates hourly demand for a circuit and will handle an unlimited number of occupancy types with no size limits or limits on data variation within the user types.

HTGUSE is the basic program that calculates space heating requirements for buildings based on weather conditions in the area. In addition to traditional methods of heat loss, the program allows two temperature setbacks. The program adjusts occupancy load gains and lighting load gains according to setback periods and also calculates the additional heat required to overcome building inertia after setback periods.

TOTDHW is the powerful hybrid of COMHWUSE and HTGUSE. It can handle an unlimited number of entries generating a circuit of any combination of users. Printout options include individual data confirmation to cumulative charts of hourly/monthly use and annual projections of space heating and domestic hot water demand. Using REDUXX data, actual daily usage can be simulated to better establish actual storage and topping economics.

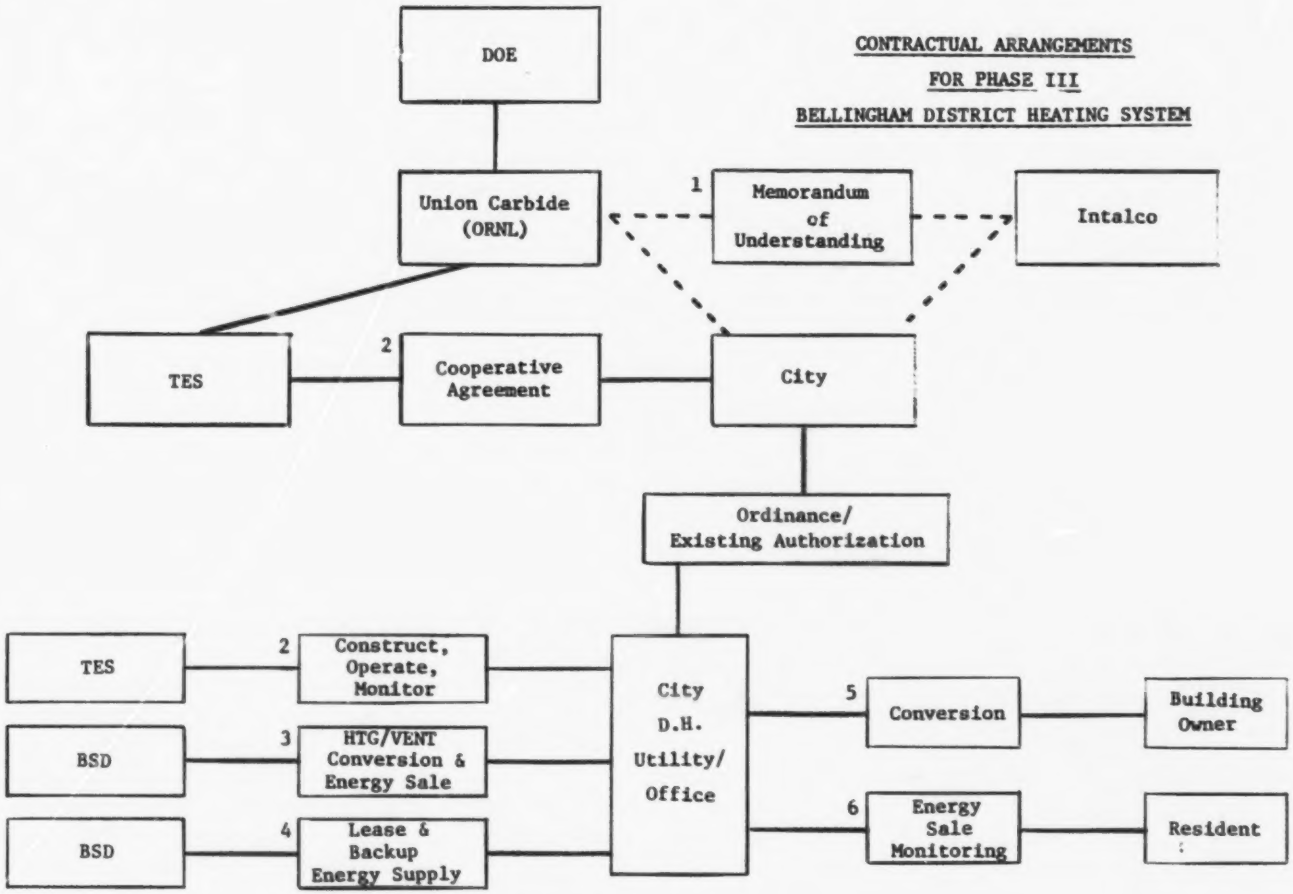
Financing Techniques

State District Heating Legislation

In order to facilitate system financing, Trans Energy Systems provided technical support to the State Senate and House Energy and Utility Committees in drafting model state district heating legislation (SSB 3033). The proposed legislation not only clarifies the authority of municipal corporations to own and operate district heating systems, but ensures the availability of revenue and general obligation bonds while providing security measures for the financing. After narrowly missing passage, the bill has been revised in meetings with Trans Energy Systems, the City of Bellingham, private utilities, bond counsel, investment bankers and key legislators, and has excellent prospects for passage in the next legislative session.

Purchase and Sale Contracts

The contracts governing the obligations and responsibilities of the parties of a district heating system are identified in Figure 1 and Table 1. After detailing the roles of Trans Energy Systems and the City in the design, construction and operation of the test system in a Cooperative Agreement as required in the Memorandum of Understanding between Union Carbide, the City and Intalco, Trans Energy Systems developed contracts between the City and energy suppliers and the City and energy purchasers. These contracts are essential for securing financing.



CONTRACTUAL ARRANGEMENTS
FOR PHASE III
BELLINGHAM DISTRICT HEATING SYSTEM

DOE
Union Carbide (ORNL)
1
Memorandum of Understanding
Intalco
TES
2
Cooperative Agreement
City
Ordinance/ Existing Authorization
TES
2
Construct, Operate, Monitor
BSD
3
HTG/VENT Conversion & Energy Sale
BSD
4
Lease & Backup Energy Supply
City D.H. Utility/ Office
5
Conversion
Building Owner
6
Energy Sale Monitoring
Resident

Legend ORNL = Oak Ridge National Laboratories
TES = Trans Energy Systems, Inc.
BSD = Bellingham School District

Figure 1

BEST DOCUMENT AVAILABLE

Table 1

BELLINGHAM DISTRICT HEATING SYSTEM AGREEMENT STATUS

PRIORITY	PARTIES	SUBJECT	STATUS
1	Union Carbide, City, and Intalco	Memorandum of Understanding Coordination of efforts of parties over Phase III heat exchanger evaluation and heating system technology development	E 12/1/80
2	TES and City	Cooperative Agreement Obligations of parties for heating system Technology development - Design, construction, operation, and restoration	E 6/11/81
3	City and B.S.D.	Conversion of B.H.S. heating and ventilation system and purchase and sale of thermal energy	D_2
4	City and B.S.D.	Lease of B.H.S. boiler room and purchase and sale of backup thermal energy	D_2
5	City and Building Owner	Conversion and restoration of space and domestic water heating system to district heating system	D_2
6	City and Resident	Purchase and sale of thermal energy; monitoring	D_2

Legend:
City = City of Bellingham
TES = Trans Energy Systems, Inc.
B.S.D. = Bellingham School District
B.H.S. = Bellingham High School
E = Executed
D = Draft
D_2 = Second Draft

Contracts with a potential energy supplier and user, the Bellingham School District, cover conversion and energy purchase by the Bellingham High School, lease of space and sale of backup energy. The School District staff, as well as independent consultants retained by the School District, have provided input on the contracts.

Contracts governing heating system conversion and purchase and sale of energy between the City and other potential customers have also been drafted. These contracts, and the proposed legislation, establish an institutional framework that facilitates financing and implementation of a district heating system and are applicable as models for any political jurisdiction.

CONCLUSION

District heating using "heats of opportunity" can provide a national savings of 5 to 8 quads of energy by the year 2000. Reclamation and distribution of waste heat through thermal energy storage/district heating systems are thus a logical candidate for development. This project will provide data to optimize system configuration and components, refine analysis techniques, and develop administrative and financing methods. By analyzing specific approaches such as Bellingham, guidelines will be established that allow municipalities and institutions to evaluate their true district heating potential.

PROJECT SUMMARY

Project Title: TES Technology Transfer in the Pulp and Paper Industry

Principal Investigator: Howard Edde, Ph.D., P.E.

Organization: Howard Edde, Inc. Consulting Engineers
1402 - 140th Place N. E.
Bellevue, Washington 98007

Project Goals: The collection and dissemination of TES system technology for the pulp and paper industry with the intent of reducing fossil fuel usage.

Project Status: The project data gathering has been completed and analyzed. The final report has been prepared, reviewed by ORNL and the TAPPI (pulp industry association) energy committee, and the final copy is in production. Papers disseminating the project results have been presented at several conferences and published as a feature article in the September 1981 issue of TAPPI magazine. One special one-day seminar disseminating the findings has been held in Portland, Oregon and another is scheduled during October in Atlanta, Georgia. A six page brochure summarizing the key information has been printed and an exhibit display constructed for use at technical meetings and trade shows. The project findings have shown that TES systems are widely used in the Scandinavian pulp and paper industry. Presently the U.S. pulp and paper industry has only two known TES installations operating which are saving about 18,000 barrels of oil per year. However by the year 2000 it is estimated that approximately 100 TES systems will be operating in U.S. mills saving approximately 1.5 million barrels of oil annually.

Contract Number: 86X-95003C

Contract Period: May 6, 1981 through September 30, 1981

Funding Level: $39,726

Funding Source: Oak Ridge National Laboratories

TES TECHNOLOGY TRANSFER IN THE PULP AND PAPER INDUSTRY

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ABSTRACT

Thermal energy storage (TES) is a technique whereby energy can be temporarily stored in order to more uniformly balance steam generation with steam demands. The pulp and paper industry accomplishes this in an accumulator using hot water or steam as the transfer medium. An international study was conducted which showed that TES is presently more universally practiced in Scandinavian mills than in U.S. mills. However, TES offers significant benefits in energy conservation, provides an instant steam reserve to stabilize mill steam demand, prolongs power boiler life, and permits displacement of oil with potentially less expensive and more abundant alternative fuels. The capital pay back time (PBT) is two to three years with return on investment (ROI) of 30 to 50 percent. Projections indicate that installed TES systems will become increasingly common in U.S. mills in the near future.

INTRODUCTION

The total steam demand placed on the boilers of a pulp mill can vary continuously. These variations can be very rapid and of signifciant magnitude. The swings in the steam demand are caused primarily by the on/off operation of batch processes in the mill. Figure 1 shows a typical batch digester steaming cycle which illustrates a unit operation with this type of variable steam demand. In mills having multiple batch digesters, it is possible the steaming demand of multiple units may coincide with a resultant extremely sharp rise in steam demand. Similar steam variations exist in other process operations within the mill.

A key consideration in evaluating steam balances and the applicability of TES is the rate, duration and frequency of steam demand variations. Mills with continuous process experience variations which are relatively less frequent but large in magnitude and duration. TES is not practical for these mills.

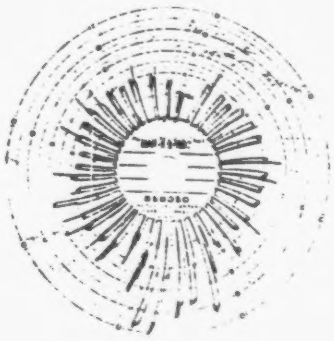

Fig. 1. Pulp Mill Batch Digester Steam Consumption

BASIC EQUIPMENT

Most mills find it advantageous to operate several boilers (recovery, hog fuel, oil, etc.) with all but one loaded at a constant level. The output of the remaining boiler is varied to match the fluctuations in the steam demand. This boiler is called a swing boiler, and is often fired by oil so that it can respond quickly. In many mills, the output of the swing boiler varies from maximum capacity to minimum capacity.

A TES system has the potential to meet these short-term energy variations which may typically last only 15 to 30 minutes. A previous Department of Energy Study recognizes the pulp and paper industry as the industry having the greatest potential for early implementation of TES systems.

The accumulator may operate either on a varying pressure or constant pressure principle. The varying pressure accumulator stores and releases steam by varying the temperature and pressure in the accumulator; the water level remains relatively constant. The constant pressure accumulator maintains a constant temperature and pressure is the vessel. Thermal energy is stored and discharged by varying the mass of water contained in the accumulator. Figures 2 and 3 show schematic flow diagrams of a varying pressure and constant pressure accumulator, respectively.

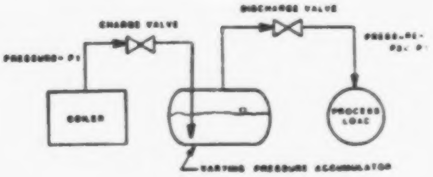

Fig. 2. Steam Storage with Variable Pressure Accumulator Principle.

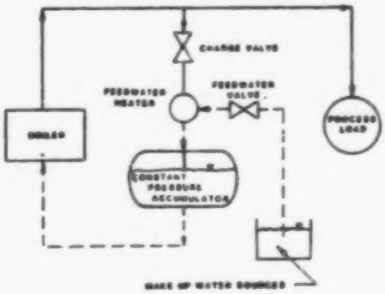

Fig. 3. Steam Storage with Constant Pressure Accumulator Principle.

CASE STUDY OF PRACTICAL APPLICATIONS

TES Integrated with Boiler Feedwater Heating

One of the most common and practical types of TES systems are those integrated into boiler feedwater systems. In these systems, the feedwater deaerator/accumulator is significantly increased in size. The large accumulator volume is used to modulate steam demands by varying the rate of feedwater heating. The amount of heated feedwater in the accumulator is allowed to vary within a set operating range.

Mill A is an integrated pulp and paper mill which uses a boiler feedwater TES system. The pulp mill produces 142,000 ADMTA of dissolving sulfite market pulp. The paper mill produces 245,000 air dried metric tons per year (ADMTA), of machine-finished news and super-calandered journal papers on two large machines. The paper mill uses baled market pulp. The mill's steam load is supplied by four boilers: a recovery, coal-fired, hog-fueled and oil/hog-fired boiler. The TES application is mostly connected with the operation of the coal boiler, which operates as a control boiler.

The TES system has been developed over the last 15 years to even out fluctuations in the process steam demand which are primarily caused by the batch digesters and paper machines. It consists of a constant pressure, closed horizontal accumulator (Accumulator I) meant mostly for batch digesters and two atmospheric pressure, warm water tanks (Accumulator II) meant mostly for the paper machines. Both systems are connected in series with each other as shown in Figure 4.

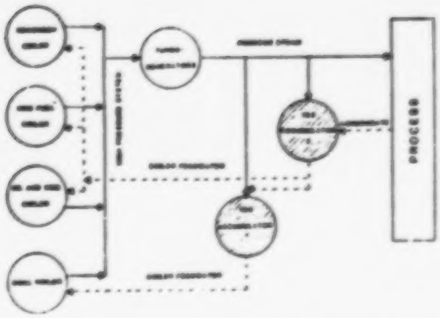

Fig. 4. Mill A TES System Flow Diagram.

Accumulator I delivers hot feedwater to the coal boiler. This steam accumulator is used to even out the steam demand from the mill's 12 batch digesters. Each cook requires a heightened steam supply for approximately one hour. There is one swing of approximately 20 t/hr in the steam demand each hour. The operation of Accumulator I is controlled by an IBM 1800 computer, and is synchronized with the batch digester cooking cycles.

Accumulator II consists of two tanks, vented to the air. Heated water from Accumulator II is delivered to Accumulator I and other boiler feedwater systems. Accumulator II is used to even out the steam demand from the paper machines. Machine tears (paper breaks) occur approximately four times per day; each tear is about 20 minutes in duration. Each time about 30 t/hr of steam is available for Accumjlator II. The pulp drying machine stops approximately once a week for two hours each time and then 30 t/hr of steam is available for Accumulator II.

The TES system provides an increased supply of steam from the coal boiler of apprxoimately 10 t/hr (22,000 lb/hr) during a six-month period of each year. The use of hog fuel (bark) has increased only slightly due to the TES system. The savings realized by the TES system were evaluated by comparing them to a hypothetical condenser system. The energy savings corresponded to 3.3 t/hr (7,300 lb/hr) of steam or 7.2 GJ/hr (6.8 million BTU/hr) of energy. This corresponds to an equivalent oil consumption reduction of ≈0.2 t/h (≈1.3 bbl/hr) based on an 89 percent boiler efficiency. Based on an oil cost of $31.40/bbl, the savings are $330,600 per year. Because the mill uses coal rather than oil, the TES system's profitability calculations were based on savings in coal use. The above energy savings corresponds to 0.33 t/hr or 2,673 t/yr of coal. The price of coal at Mill A is $64/t, thus the TES savings is $171,000 per year. An engineering cost estimate was prepared of the installed equipment based on 1980 dollars for use in profitability calculations. The estimated installed capital cost was $450,000 with estimated fixed operating costs of $9,000 per year. The calculated pay back time is 2.8 years and the return on the investment is 31 percent.

Recent trends in the U.S. pulp and paper industry indicate there are an increasing number of mills converting from oil-fired boilers to coal-fired ones. TES systems are particularly valuable in mill configurations where coal boilers are used as control boilers. The dynamics of oil-fired boilers allow rather rapid changes in steam production. However, the response time of coal boilers are significantly slower. TES systems can be used, as described in this case example, to buffer the rapid swings in steam demand to match the response rate of a coal boiler and achieve much better process control. This concept can also be utilized on hog fuel boilers.

Mill TES System and Local District Heating

Many pulp mills in Scandinavia and the United States are located near or within communities. Many of these communities (in Scandinavia) operate district heating systems. District heating systems are expected to become increasingly common in the United States. This case example mill is unique in that its TES system provides heat to the community district heating system, thereby providing an advantageous symbiotic energy conservation relationship useful to both the mill and the community.

The mill is an integrated pulp and paper facility. Both Kraft and sodium sulfite pulps are produced: 160,000 ADMTA and 80,000 ADMTA, respectively. Cross recovery of chemicals is practiced. The paper mill, with five paper machines, uses all the Kraft pulp and ten percent of the sulfite pulp to produce Kraft and sack paper. The balance of pulp is sold to other mills. There is no bleach plant or pulp dryers. The power plant includes seven boilers. However, the load is primarily carried by the recovery boiler and a hog/oil-fired boiler. Swings in the steam demand are met by varying the oil-firing rate. The other boilers are run at a relatively constant rate. The mill generates 46 MW (88 percent) of its electrical energy requirements. There are three turbo-generators, one back pressure turbine, one extraction, back pressure turbine and a condensing turbine. The condensing turbine serves as a spare.

The TES system includes a 430 m^3 (15,200 ft^3) constant pressure (500-700 kPa [70-100 psia]) accumulator, two U-tube heat exchangers and the connecting piping and controls. The vertical accumulator operates on the principle that hot water in the upper part and warm water in the lower part of the accumulator do not mix with one another.

The TES system is charged by heating water in the heat exchangers with low pressure steam as shown in Figure 5. Water is pumped from the bottom of the accumulator through the heat exchangers to the top of the accumulator. The accumulator is discharged by pumping water from the top of the accumulator to the district heating system. New water is added only to replace the water that leaks from the district heating system. Water can also go straight from the heat exchangers into the district heating system.

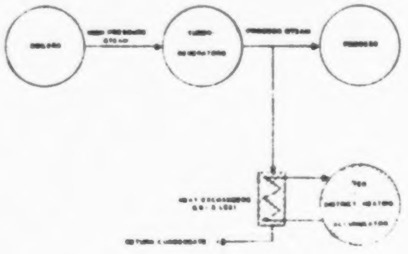

Fig. 5. Mill C TES System Flow Diagram.

Variations in steam demand come mostly from the cooking departments (batch digesters) and the five paper machines. The operation of the sulfite and Kraft cooking departments is not synchronized. Variations in steam demand from the two cooking departments are often superimposed on each other, causing significant load swings on the power plant. Feedwater heating for the recovery boiler also causes disturbances in steam demand because it receives all the fresh feedwater to the power plant and the flow rate of this feedwater varies.

The thermal energy storage system began operation in 1980. In five years the mill will be supplying 180 GJ/hr (170 million BTU/hr) to the district heating system. This would represent about 85 percent of the district heating demand. At the present time only about 7.2 GJ/hr (6.8 million BTU/hr) are being demanded by the district heating system, but this is to rise within a year to 25.2 GJ/hr (23.9 million BTU/hr). Even though the district heating load has been small, most of the potential benefits of the TES system have been realized.

The TES system has provided an estimated reduction in oil consumption of ≈20,000 barrels of oil per year. Most of this reduction, ≈16,000 barrels, was obtained by a shift from oil to hog fuel. It is important to realize that the boiler dynamics did not permit rapid changes in the hog fuel firing rate; thus, oil was required to meet the original swinging steam demands. Installation of the TES system modulated the swings such that significantly larger quantities of hog fuel could be burned.

The value of the savings obtained as a result of the TES was estimated to be ≈$295,500 per year. The savings were estimated to be $183,400 per year when savings from the oil displaced by hog fuel were not included. The installed cost of the TES system is estimated to be $560,000 in 1980 dollars. In addition, the district heating system modifications were estimated to be $570,000. The pay back time (PBT) is 2.0 years and the return on investment (ROI) is 46 percent, when the savings from the disposition of oil with hog fuel are included in the analysis.

What makes this TES application unique and particularly interesting is the fact that it is coupled with a district heating system. The investment analysis of this application versus other industrial applications indicates the TES costs and benefits are quite similar. An advantage of this district heating application is that there is a quite large sink that aids in the operation of the TES system. Each mill is unique; thus, the applicability and profitability of the TES system is dependent on case-by-case conditions.

PROJECT SUMMARY

Project Title: Thermal Energy Storage Systems for Industrial Process and Reject Heat Applications

Program Manager: R. T. Waibel

Organization: Institute of Gas Technology
IIT Center
Chicago, Illinois 60616

Project Goals: Research and development of advanced high-temperature thermal energy storage media and TES subsystem for industrial process applications.

Project Status: SIC-32 industry (brick, ceramic, clay products, and refractories) selected for initial assessment of energy savings, economics, and technical feasibility of advanced composite latent/sensible heat media. Carbonate/ceramic composite powder processing, shape fabrication, and initial media stability tests are in progress.

Future activities include —

- Continuing media processing, fabrication, and stability testing
- Perform media thermophysical and mechanical property measurements
- Conduct lab-scale and engineering-scale TES performance tests
- Develop analytical TES performance model
- Assess technical, economic, and energy savings impact of advanced TES integration in ceramic periodic kiln system.

Contract Number: ORNL/UCC 86X-9500-1C

Contract Period: May 1, 1981 through April 30, 1982

Funding Level: $1,204,184

Funding Source: U.S. Department of Energy through Oak Ridge National Laboratory

ADVANCED HIGH-TEMPERATURE THERMAL ENERGY STORAGE MEDIA FOR INDUSTRIAL APPLICATIONS

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ABSTRACT

An advanced thermal energy storage media concept based on use of carbonate salt/ceramic composite materials is being developed for industrial process and reject heat applications. This paper describes the composite latent/sensible media concept and its potential advantages over state-of-the-art latent heat systems. Media stability requirements, on-going materials development efforts, and planned TES performance evaluation tests are discussed.

INTRODUCTION

Work conducted under previous TES development programs at IGT has demonstrated the attractive properties and stability of alkali metal/alkaline earth metal carbonates as latent-heat phase-change storage media, as indicated in References 1-5. Various carbonate compositions having melting points covering the range from 397°C to 898°C have been evaluated for materials compatibility and TES performance as free melts in shell-and-tube HX configurations utilizing austenitic stainless steel or nickel-base superalloy materials of construction. An engineering-scale TES module of 25,000 Btu thermal capacity (latent plus sensible) has also been designed, fabricated and tested with 130 lb of $LiKCO_3$ salt, which melts congruently at 505°C with a heat-of-fusion of 148 Btu/lb. The module showed very stable thermal performance and excellent compatibility between salt and AISI 316 stainless steel containment and HX tube during 5650 hours of testing and 129 charge/discharge cycles over the temperature range 480° to 535°C. Although the 300-series austenitic stainless steels have been found to be generally compatible with molten carbonates at temperatures up to 700°C, superalloys or coatings are required for long-term operation at higher temperatures, significantly increasing the cost of a TES subsystem.

In-house work conducted at IGT has demonstrated the feasibility of an alternative approach to containing molten carbonates which will, when successfully developed, allow elimination of HX tube configurations and operation in direct contact with compatible working fluids. This approach thus offers potential for significant cost reductions through elimination of HX tube materials and fabrication costs, as well as improved thermal performance via direct-contact operation.

DESCRIPTION OF ADVANCED MEDIA CONCEPT

This advanced composite medium consists of a phase-change carbonate salt (latent-heat phase) supported and immobilized within the submicron-sized capillary structure of a particulate ceramic matrix or porous sintered ceramic (sensible-heat phase).* Immobilization of the molten salt within the porous ceramic structure permits operation of the composite pellets, bricks, or other suitable shapes in direct contact with compatible fluids, thus eliminating expensive heat-exchanger tubes required in shell-and-tube HX designs. Such a direct-contact HX design could consist of composite media shapes fabricated as cylindrical pellets, briquettes, spheres, etc. and utilized in a packed-bed arrangement. Figure 1 is a photograph of typical composite media pellets pressed from a carbonate/ceramic powder mixture. Alternatively, composite materials could be formed as brick shapes and stacked in a regular array similar to a checkerwork regenerator.

ADVANCED MEDIA RESEARCH AND DEVELOPMENT APPROACH

The composite media are being developed to operate in direct contact with industrial process gases during thermal charging and discharging. The phase-change salts are being selected from available alkali metal/alkaline earth metal carbonates and their mixtures (latent-heat phase), which are attractive for utilization in this direct-contact HX concept because of their superior high-temperature chemical stability and low vapor pressures in air and other oxidizing gases containing CO_2, O_2, and H_2O. Numerous congruently melting salt mixtures based on the alkali carbonates Li_2CO_3, Na_2CO_3, and K_2CO_3 are available with melting points covering the range 397°C (Li_2CO_3-Na_2CO_3-K_2CO_3 ternary eutectic) to 898°C (pure K_2CO_3), as summarized in Table 1. Candidate carbonates are being selected primarily on the basis of melting point, heat of fusion, cost, and thermochemical stability, although other properties such as density, volume change on fusion, heat capacity, thermal conductivity, viscosity, and surface tension are also being evaluated. Emphasis is being given to compositions based on Na_2CO_3 because of its attractive heat-of-fusion (114 Btu/lb), heat capacity (0.40 Btu/lb-°F) and low cost as a technical-grade salt ($0.03/lb). The congruently melting sodium carbonate-based compositions under consideration include Na_2CO_3-Li_2CO_3 (496°C m.p.), Na_2CO_3-$BaCO_3$ (686°C m.p.), Na_2CO_3-K_2CO_3 (710°C m.p.) and Na_2CO_3 (858°C m.p.). Incongruently melting compositions are also considered in the Na_2CO_3-Li_2CO_3 and Na_2CO_3-K_2CO_3 systems as a means of "tailoring" thermal and physical characteristics.

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* IGT has filed a patent application on this concept.

The ceramic support materials (sensible-heat phase) are being selected primarily from metal oxides, aluminates, ferrites, or titanates. The functions of the ceramic phase are to provide stable capillary forces for retention of the molten carbonate phase and to contribute sensible heat to the composite media. The most critical property of the ceramic support material is expected to be its chemical stability in the high-temperature carbonate environment. Significant chemical reaction or solubility of the ceramic in the molten carbonate will affect the long-term carbonate retention property and structural integrity of the composite. Other selection criteria for the ceramic support material include specific heat, cost, and ability to prepare as fine particulates or porous bodies.

Composite carbonate/ceramic powders are prepared from aqueous slurries using a spray drying process, which produces homogeneous, intimately dispersed powders with excellent flowability and forming characteristics. Spray-drying process procedures are being developed for preparation of ceramic supports and composite powders with controlled properties satisfying TES functional requirements. These materials are characterized with respect to critical properties such as chemical composition, specific surface area of support, particle size and shape distributions, flowability, and forming characteristics.

Efforts are also in progress in the area of composite shape fabrication. Laboratory studies of pellet pressing in steel dies are being used to guide the selection and development of ceramic-forming processes for cost-effective mass production of composite shapes. Commercial vendors with significant experience in ceramics fabrication are being utilized to perform experimental feasibility and appropriate development studies of processes such as automatic dry powder pressing, extrusion, briquetting, and pelletizing.

Materials screening tests are being conducted to identify and resolve technical issues related to media compatibility and long-term stability under simulated industrial TES service conditions. Thermogravimetric analysis measurements are used to detect and quantify media/gas interactions such as vaporization, carbonate decomposition, or reaction of carbonate or ceramic phases with gas constituents. The P_{H_2O}/P_{CO_2} ratio and impurity levels of sulfur, chlorine, and fluorine-containing species in the gas environment are expected to affect carbonate/gas interactions and are being experimentally evaluated.

Isothermal aging tests are conducted by exposing candidate media pellets to simulated process gas environments at temperatures above the carbonate melting point. Specimens are removed at pre-selected time intervals and characterized with respect to shape retention, physical or chemical changes in ceramic support particles, loss of carbonate, and changes in chemical composition.

Thermal cycling tests are focusing on overall stability of candidate composite media during repeated cycling through the carbonate phase-change temperature. Pre- and post-test physical and chemical analyses of the media are used to evaluate thermal shock resistance, shape retention, and carbonate retention of the media. In addition, cycling tests will be conducted on a packed bed of media shapes to identify potential problems associated with changes in bed configuration, packing density, gas flow resistance, thermal ratcheting, etc.

Additional materials compatibility screening tests will be conducted by exposing specimens of containment, piping, and insulation materials in contact with the candidate carbonate/ceramic media in high-temperature air furnaces. Specimens will be removed at various time intervals and characterized with respect to corrosion reactions and overall physical/chemical stability.

The results of the screening tests will be used to finalize the selection of media compositions, processing/fabrication techniques, and other TES component materials for TES charge/discharge testing in laboratory-scale modules.

Some critical gaps exist in the data base of thermal, physical. and mechanical properties for candidate carbonates and ceramics that are required for adequate evaluation and development of the composite media concept. Relevant thermophysical property data for the carbonates and ceramics are being reviewed and evaluated. Additional required property measurements are being performed either in IGT's laboratories or by competent outside laboratories. As required, high-temperature compressive strengths and creep behavior of composite media will be measured to assure structural integrity of the media under service conditions in the reference TES system design. Similarly, four-point bending strengths will be measured at room and elevated temperature, as required, to determine composite fracture strength and to identify key materials characteristics and processing parameters that control media strength and thermal shock resistance.

Laboratory-scale TES charge/discharge performance tests will be conducted on the most promising composite media compositions, shapes, processing/fabrication techniques, and other subsystem components.

Laboratory-scale TES modules are being designed and constructed to minimize heat losses to ambient and will be adequately instrumented to provide reliable and detailed data for evaluating efficiency, radial and axial temperature distributions, solid/gas heat-transfer coefficients, flow rates of charge/discharge gases, flow distribution, and pressure drops through the media bed. The system will be charged and discharged using air heated by an electric heating element.

An analytical computer model is being developed to describe the thermal and hydraulic performance of a TES subsystem containing a packed bed or array of composite latent/sensible media shapes. The model will consider media thermal and physical properties, shape, size, arrangement, and packing density; physical dimensions of TES module; transport properties of working fluid; and other significant physical and operating parameters.

Sensitivity studies will be performed with respect to media properties and TES system design characteristics to identify the most significant parameters controlling system performance, efficiency, and cost and to guide future design optimization efforts.

INDUSTRIAL APPLICATIONS

The advanced media development and TES testing results will provide a significant data base relevant to a broad range of high-temperature industrial storage applications, including the metallurgical, ceramics and refractories industries. The initially targeted TES application is in the SIC-32 industries (brick, ceramic, clay products, and refractories) which use periodic kilns exhausting high-temperature (250° to 1100°C) flue-gases.

Approximately half of the firing kilns in SIC-32 industries are periodic in nature and well-suited to integration with thermal energy storage. Figure 2 shows 1975 levels of fuel consumption in SIC-32 categories. Implementation of TES could result in ∼45% energy savings for a typical periodic kiln installation and a total SIC-32 industry annual energy savings of 0.2 quad. Further analyses will be performed to further refine assessments of energy savings, cost-effectiveness, and environmental acceptance of an advanced TES system in this industry category.

Typical operation of a periodic kiln involves a heat-up stage, a soaking stage, and a cooldown stage as depicted in Figure 3. During the first two stages, hot flue-gases can be routed to a TES device; during the cooldown stage heated air passing over the hot product can also be routed to the TES device. Thus, the TES unit is charged thermally with heated gases that are normally vented to the ambient. Three possible uses of the heat stored in the TES unit are –

1. Preheating of combustion air to 540°C and above. For SIC-32 industrial operating conditions, air preheating can mean a 25% fuel reduction.

2. Preheating kiln ware up to 540°C prior to firing of kiln burners.

3. Greenware drying, utilizing heat from the TES unit in the 25° to 85°C temperature range. All of the energy normally input to the dryers can be obtained from the TES device, thus saving as much as 50% of total plant fuel consumption.

A centrally located TES unit divided into several modules can be designed to accept heat from several sources and reject the heat to other heat-requiring operations within the plant. Figure 4 shows a 2 kiln/1 dryer brick plant incorporating a TES unit consisting of one TES module per heat-using device. Such a system requires high temperature ductwork and valves, blowers, and a control and instrumentation scheme to optimize heat usage.

Exhaust gases from these kilns typically contain sulfur oxides, fluoride, and chloride impurities, and particulates, depending on the product line and the fuel used (natural gas, coal, oil, or sawdust). A literature survey and in-plant measurements of industrial gas compositions and impurity levels are planned to define the operating environments with which the advanced composite media must be compatible.

CONCLUSION

Materials development and laboratory evaluations of an advanced composite latent/sensible TES media are in progress. Successful development and scale-up of this concept are expected to provide a TES technology base for energy savings in numerous industrial processes.

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3. Maru, H. C., et al., "Molten Salt Thermal Energy Storage Systems," COO-2888-3. Chicago: Institute of Gas Technology (NASA-CR135419, 1978), March 1978.

4. Petri, R. J. et al., "High-Temperature Molten Salt Thermal Energy Storage Systems." Chicago: Institute of Gas Technology (NASA-CR159663), February 1980.

5. Petri, R. J., Claar, T. D., and Marianowski, L. G., "High-Temperature Molten Salt Thermal Energy Storage Systems for Solar Applications," NASA Final Report in preparation.

Table 1. CONGRUENT MELTING CARBONATE COMPOSITIONS

Composition, wt %	m.p., °C (°F)	ΔH_f, Btu/lb	Cost, $/lb*	Btu/$†
$32Li_2CO_3-33Na_2CO_3-35K_2CO_3$	397 (747)	119	0.46	259
$46.6Li_2CO_3-53.4K_2CO_3$	488 (910)	168	0.67	251
$44.3Li_2CO_3-55.7Na_2CO_3$	496 (925)	169	0.55	307
$28.5Li_2CO_3-71.5K_2CO_3$	498 (928)	136	0.48	283
$35.0Li_2CO_3-65.0K_2CO_3$	505 (941)	148	0.55	269
$55.7Li_2CO_3-44.3CaCO_3$	662 (1224)	-	0.69	-
$47.8Na_2CO_3-52.2BaCO_3$	686 (1267)	74	0.11	673
$50Na_2CO_3-50K_2CO_3$	710 (1310)	70	0.11	636
Li_2CO_3	723 (1330)	261	1.21	216
Na_2CO_3	858 (1576)	114	0.03	3800
K_2CO_3	898 (1648)	86	0.19	453

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* Costs from Chemical Marketing Reporter, June 16, 1980.

† Based on heat-of-fusion only; sensible heats neglected.

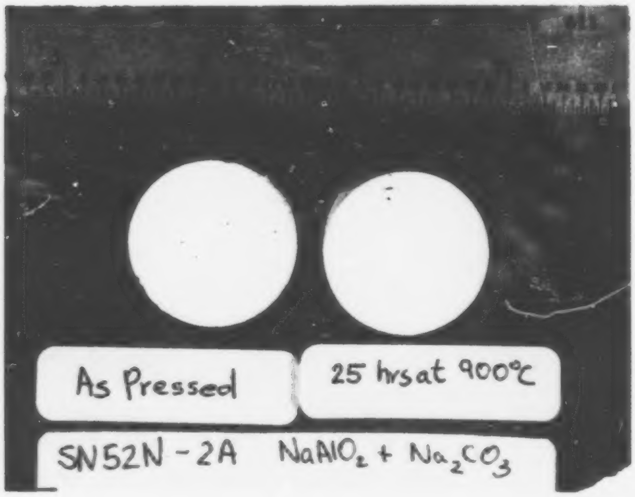
As Pressed
25 hrs at 900°C
SN52N - 2A NaAlO₂ + Na₂CO₃

Fig. 1. Composite Pellets of Na_2CO_3/$NaAlO_2$ Particulates
Left: As cold-pressed
Right: Heated at 900°C for 25 hours

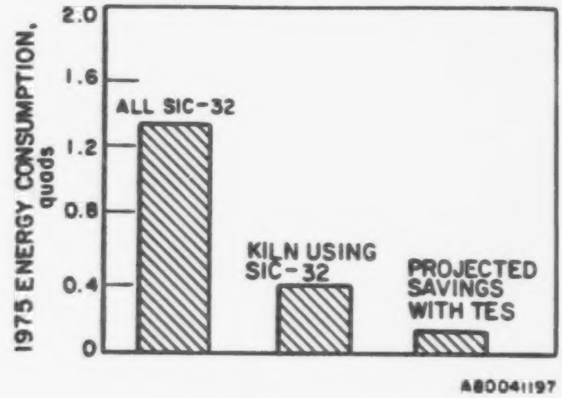

Fig. 2. 1975 Energy Consumption in SIC-32 Industries and Projected Savings With TES

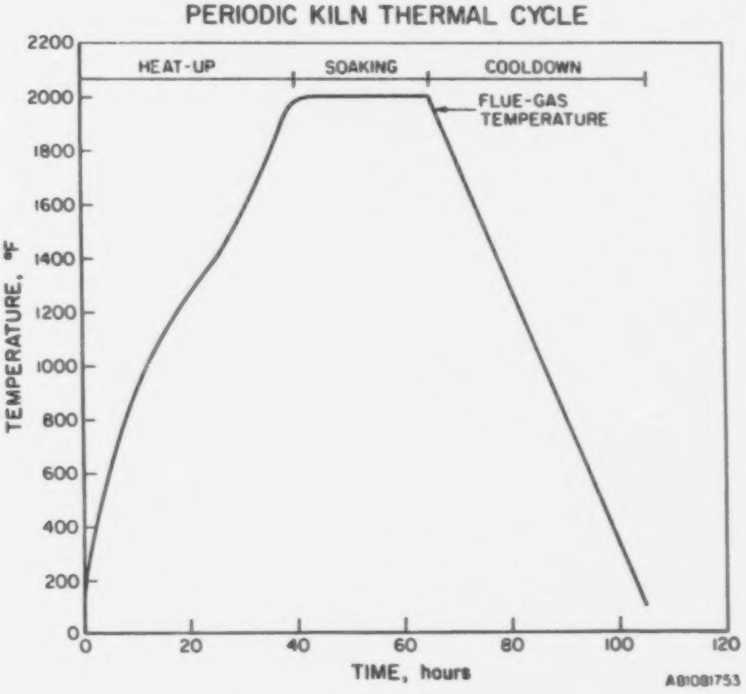

Fig. 3. Typical Thermal Cycle of Periodic Kiln

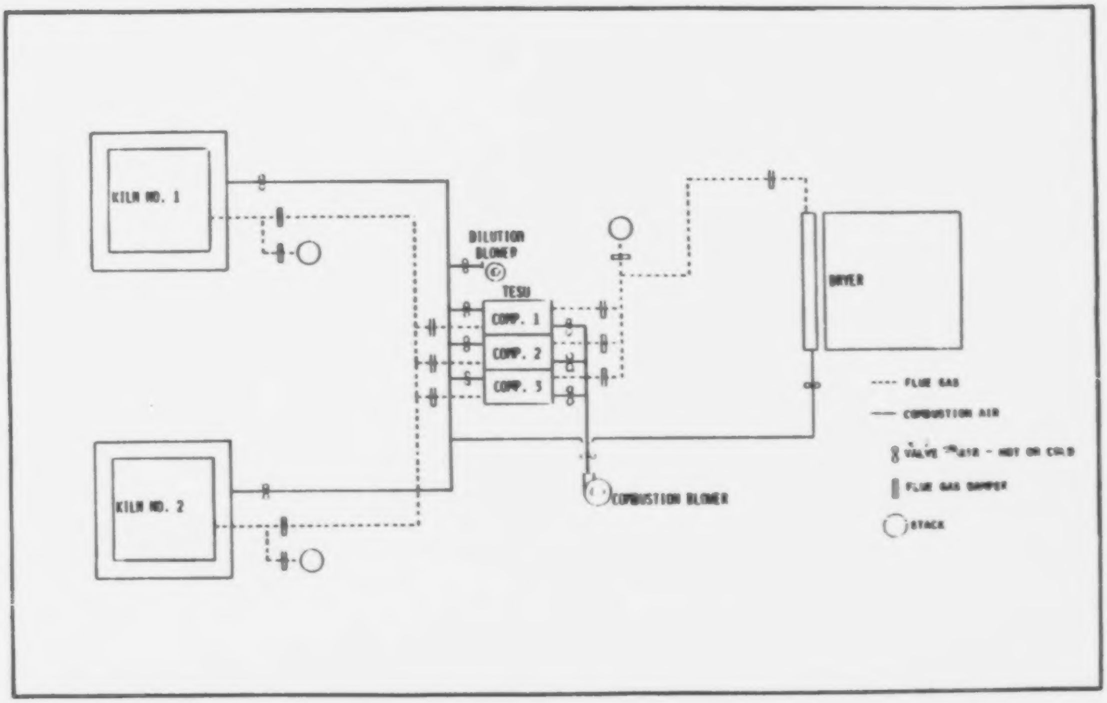
KILN NO. 1
KILN NO. 2
DILUTION BLOWER
TESU
COMP. 1
COMP. 2
COMP. 3
COMBUSTION BLOWER
DRYER
FLUE GAS
COMBUSTION AIR
VALVE - AIR - HOT OR COLD
FLUE GAS DAMPER
STACK

Fig. 4. Schematic of TES System in Periodic Kiln Application

SANDIA NATIONAL LABORATORY SOLAR THERMAL APPLICATIONS

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PROJECT SUMMARY

Project Title: Molten Nitrate Salt Technology Development for Central Receiver Applications

Principal Investigators: S. H. Goods

Organization: Sandia National Laboratories
Livermore, CA 94550

Project Goals: Develop the technology base required for the successful application of molten nitrate salts as a heat transfer and thermal energy storage medium in Solar Central Receiver Systems.

Project Status: This project spans numerous technical disciplines and topical reports are published when appropriate. During this reporting period, the following reports were issued:

> D. A. Nissen, "A Single Apparatus for the Precise Measurement of the Physical Properties of Liquids at Elevated Temperature and Pressure," Sandia Laboratories Report SAND80-8034, October, 1980.
>
> D. A. Nissen, "Thermophysical Properties of the Equimolar Mixture NaNO$_3$-KNO$_3$ from 300-600°C," Sandia Laboratories Report SAND80-8040, November 1980.
>
> R. W. Mar and C. M. Kramer, "Pressure-Temperature Composition Relationships for Heated Drawsalt Systems," Sandia National Laboratories Report SAND80-8043, December 1980.
>
> R. W. Bradshaw, "Corrosion of 304SS in Molten NaNO$_3$-KNO$_3$ in a Thermal Convection Loop," Sandia National Laboratories Report SAND80-8856, December 1980.
>
> R. W. Carling, el. al., "Molten Nitrate Salt Technology Development Status Report," Sandia National Laboratories Report SAND80-8052, March 1981.
>
> S. H. Goods, "Creep and the Corrosion Characteristics of Incoloy Alloy 800 in Molten Nitrate Salts," Sandia National Laboratories Report SAND81-8665, March 1981.
>
> D. A. Nissen, "The Chemistry of the Binary NaNO$_3$-KNO$_3$ System, Sandia National Laboratories Report SAND81-8006, June 1981.

Experimental activities addressing the probability of a serious salt stability or corrosion problem occurring in the short term have been completed. Future activities will address the issues of long term performance and lifetime predictions.

Contract Number: AN-35, PACE35-AL-10

Funding Level: $187,000

Funding Source: U.S. Department of Energy

MOLTEN NITRATE SALT STUDIES FOR CENTRAL RECEIVER APPLICATIONS

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ABSTRACT

This paper summarizes the experimental activities underway at Sandia National Laboratories in support of the development of solar central receiver systems utilizing molten nitrate salts for energy storage and heat transfer. The results obtained during the last year are discussed.

INTRODUCTION

Drawsalt, nominally a 50-50 molar mixture of $NaNO_3$ and KNO_3 is a leading candidate material for use as a high temperature energy storage and heat transfer medium in solar thermal power systems. Nitrate based salts are inexpensive, abundant, readily available, have excellent thermal properties and low vapor pressures. They have been used for many years in the chemicals and metals industries without problems. Extending the broad base of industrial experience to solar applications is not without uncertainty because of the more rigorous demands of solar systems. Accordingly, Sandia Laboratories has developed and implemented a plan to address uncertainties and potential problems. Our activities can be grouped into two broad areas: salt chemistry and properties, and corrosion. Results obtained during the last year are discussed in this paper.

CHEMISTRY AND PROPERTIES

Thermal Degradation

Nitrate salts, upon heating, can undergo numerous different decomposition reactions. For example, the nitrate ion can decompose to nitrite, which can further decompose to oxide, peroxide and/or superoxide. Salt degradation can also occur by interaction with atmospheric constituents such as H_2O and CO_2 to form hydroxide and carbonate. Conceptual design studies sponsored by the DOE have indicated that systems in which the drawsalt is allowed to contact ambient air are highly desirable because of cost and system design simplicity arguments. Thus, we have studied the extent to which these degradation reactions occur in an operating system where salt is in direct contact with air.

Experimental results to date have supported the agrument that the dominant reaction is

$$MNO_3 = MNO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

where M is one or a mixture of alkali metal elements. It is often proposed that one needs only to consider this reaction in the representation of salt decomposition in air. In our studies, nitrate salt was placed in gold crucibles and heated to 550°C to 600°C in flowing air. Salt samples were withdrawn periodically and analyzed by wet chemical methods. The salt composition reached a steady state value within several hours, and did not change upon further heating for an additional 60 hrs, the duration of the experiments. The final salt composition was a mixture of nitrate and nitrite. In no case was there any evidence of oxide, peroxide or superoxide. The minimum detectable level for these species was $\sim 10^{-4}$ molal.

Several long term corrosion tests have provided additional data to support the thesis that reaction (1) is dominant. An analysis of salt samples taken from thermal convection loops operating for thousands of hours exposed to ambient air showed salt compositions consistent with the reaction.

In an effort to develop a fundamental understanding of the decomposition process, vacuum decomposition studies were carried out using a thermal microbalance and evolved gas analysis system. Because these experiments were performed in vacuum, one cannot directly relate the results to the problem of greatest practical interest, namely, decomposition in air. The motivation behind the vacuum decomposition study was to gain insight into intrinsic decomposition steps, i.e. molecular decomposition reactions uncomplicated by collisions with molecules in the gaseous phase. These studies were carried out on the pure salts of $NaNO_3$ and KNO_3 over the temperature range 350-525°C. It was found that the salts completely decomposed and vaporized, i.e. the salt weight loss was total. Rates of decomposition were calculated for the initial stages of weight loss, and the results are shown on Figure 1. Activation energies associated with the vacuum decomposition of $NaNO_3$ and KNO_3 were virtually identical, 35-36 kcal.

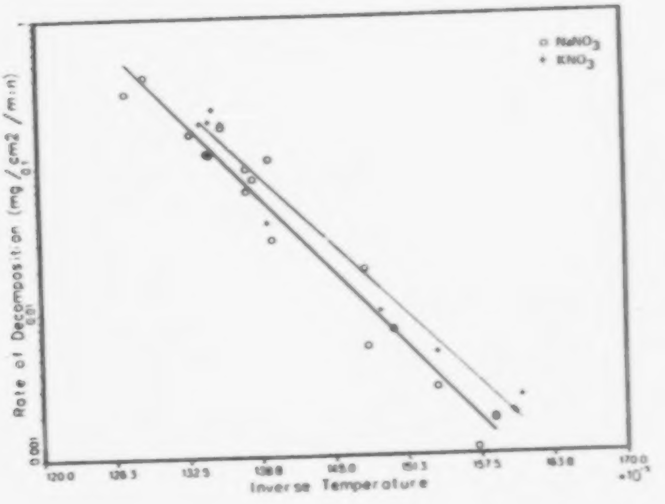

Figure 1. Initial rates of decomposition for NaNO$_3$ and KNO$_3$ as determined by vacuum thermal balance experiments.

The gases evolving from the salt during decomposition demonstrated the behavior shown in Figure 2. N_2 was always the first gas observed, followed by NO and O_2 in that order of appearance and abundance.

At first glance, it appears the vacuum decomposition results contradict Freeman's results (he observed the sample to arrest at a weight corresponding to the oxide composition) and the results discussed earlier where reaction (1) was said to dominate. However, it is known that the thermodynamically favored salt composition is very dependent upon the N_2 and O_2 partial pressure (eg. see Figure 3), and the various decomposition studies have taken place in different areas of the stability phase space.

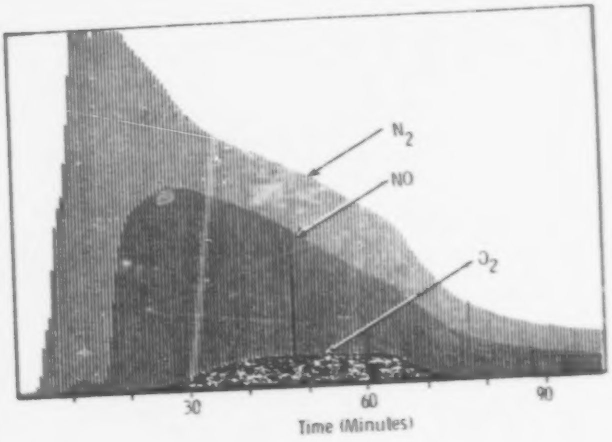

Figure 2. Mass spectra of gases evolved from NaNO$_3$ heated in vacuum at 750K.

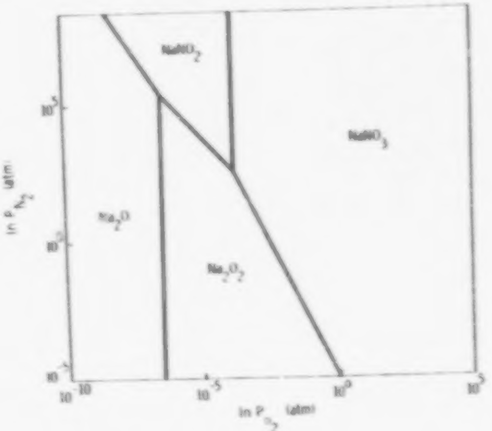

Figure 3. Phase stability diagram for the Na-N-O system at 800K.

BEST DOCUMENT AVAILABLE

Thermophysical Properties

The thermophysical properties of drawsalt, viscosity, surface tension and density, have been measured over the temperature range 275-600°C and the properties can be expressed as follows:

$$\eta(\text{cp}) = 27.714 - .120T + 2.281 \times 10^{-4}T^2 - 1.475 \times 10^{-7}T^3$$

$$\gamma(\text{dyne/cm}) = 133.12 - 6.25 \times 10^{-2}T$$

$$\rho(\text{g/cc}) = 2.100 - 6.56 \times 10^{-4}T$$

where T is the temperture in degrees centigrade.

Thermochemical Properties

The heat capacity of drawsalt has been measured over the temperature range 77° - 427°C with a differential scanning calorimeter, and the results are shown in Figure 4. These values are not in total agreement with previously reported values and the current emphasis is on resolving the discrepancies.

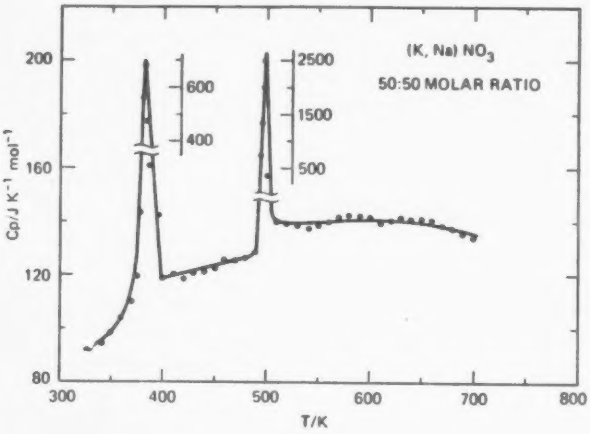

Figure 4. Heat capacity of drawsalt as determined by differential scanning calorimetry.

CORROSION

The corrosion studies at Sandia can be divided into the separate but related areas of general corrosion, environmental corrosion cracking, and galvanic corrosion.

General Corrosion

In-house studies addressed the general corrosion behavior of 304SS, 316SS, and Incoloy 800 in drawsalt. The primary experimental vehicle was the thermal convection loop; various static immersion experiments were also carried out to complement the loop tests. The status of convection loop tests are summarized in Table I.

Table I. Status of Molten Salt Convection Loop Experiments

Loop Material	Salt	Hours of Operation	Status of Test
304SS	Drawsalt	8500	Completed
316SS	Drawsalt	5500	Completed
316SS	Drawsalt	3500	Completed
I800	Drawsalt	5500	Completed
I800	Drawsalt	5000	Ongoing
316-I800-C Steel	Drawsalt	5200	Completed

The general features of corrosion are similar for all of the alloys studied. Three processes are in operation: oxidation, oxide loss due to flaking and chromium depletion. The combined effect of these three processes is a weight change curve with the general features illustrated in Figure 5. The magnitude and position of the weight change maximum and zero intercept are dependent upon the alloy system, temperature and salt composition. Data from the I800 convection loop is shown in Figure 6.

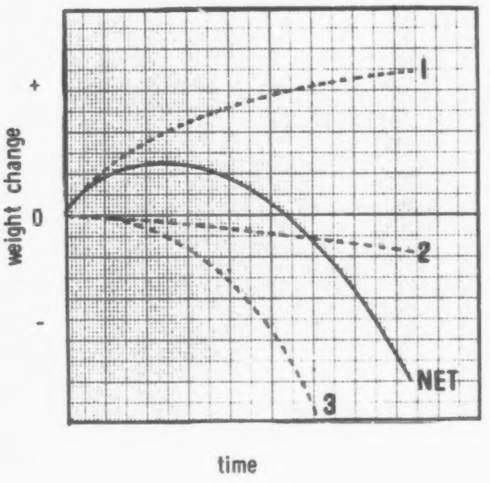

Figure 5. The general characteristics of alloy corrosion in nitrate salts. The net weight change is due to the combined effects of 1 - oxide formation, 2 - chromium depletion, and 3 - oxide flaking.

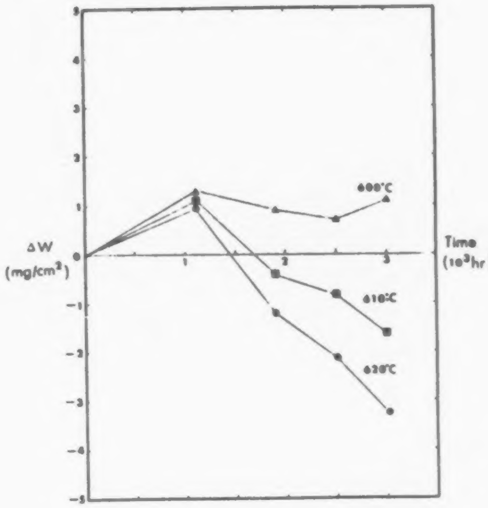

Figure 6. The corrosion of Incoloy 800 samples in molten drawsalt.

With regard to practical considerations, general corrosion has not been found to be a serious problem at temperatures below 600°C. Incoloy 800 and 316SS corrode at rates of less than 1 mil/yr and this rate is certainly acceptable. Further, there is no evidence to suggest the existence of deleterious features such as deposit formation, plugging and mass transport.

Environmental Cracking Corrosion

In the presence of an aggressive environment, applied stresses can produce corrosion effects which would not otherwise occur. A well known manifestation of this phenomenon is stress corrosion cracking. Corrosion fatigue is another problem of concern in which the effects of fluctuating stress or strain and corrosive environment are coupled. Our environmental cracking studies have concentrated on the behavior of Incoloy 800, the alloy which emerged as the leading candidate from general corrosion tests. Activities include creep, slow strain rate and fatigue crack growth testing.

The constant load, isothermal creep experiments consist of testing, either to fracture or to some predetermined strain level, salt filled I800 tubular specimens. Aside from environmental effects, the results indicate, that in the solution annealed condition, the alloy is microstructurally unstable at temperatures near 600°C. $M_{23}C_6$ carbides precipitate rapidly along grain boundaries and to some extent homogenously. While these instabilities do not preclude the use of this alloy in high temperature solar receiver applications, appropriate stabilizing heat treatments will be necessary as design parameters.

Measurements of creep ductility or time to rupture alone do not reveal an environmentally induced degradation of structural properties. Deformation does not change the mode of corrosive attack. That is, it remains a general surface corrosion problem. However, deformation does result in a thicker, more porous oxide on deformed sidewall sections compared to the oxides formed on undeformed surfaces as shown in Figure 7. This suggests that these oxides crack as a result of the imposed creep strain. This cracking results in the exposure of fresh base metal to the molten salt, with the net effect being an acceleration in the overall corrosion rate and a reduction in potential service lifetime. However, these observations of accelerated corrosion are generally associated with large strain experiments. The amount of strain anticipated in actual operating systems is small enough that the extent of "enhanced" general corrosion should not constitute a significant problem.

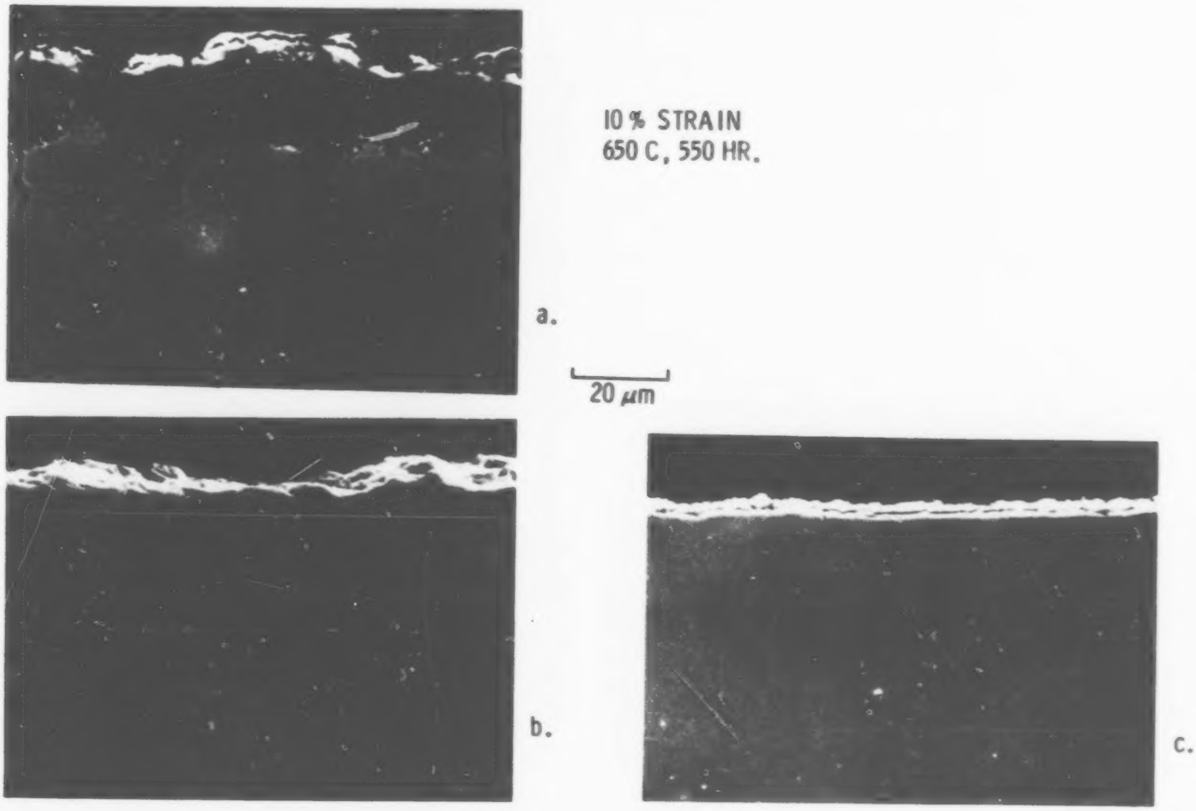

Figure 7. Oxide corrosion layers formed on Incoloy 800. a) Salt exposed sidewall (deformed), b) Salt exposed sidewall (undeformed), c) air exposed sidewall.

Slow strain rate tests have also been carried out to assess the susceptibility of I800 to stress corrosion cracking in molten salt. Experiments were performed in air and in a salt environment, and the relative differences in ductility (as measured by elongation, reduction in area, etc.) serve as an indicator of environmentally induced degradation in mechanical properties. To date, experiments have been carried out at 600°C and at strain rates of 10^{-5} - 2×10^{-7} sec^{-1}. The results have given no indication that the molten salt environment significantly affects the tensile properties of I800.

A technique to measure fatigue crack growth in molten salt at elevated temperatures has been developed. Compact tension specimens are placed in a salt bath and cycled at frequencies between 0.67 and 3 Hz. Crack growth rates (da/dN) are determined by a compliance technique using a COD gage remotely coupled to the specimen via a series of pushrods. Specimens are cycled in load control with R = .05 ($R = \Delta K_{min}/\Delta K_{max}$). Preliminary results are shown in Figure 8 where crack growth rates for Incoloy 800 at 600°C in air and in salt are compared. The data suggests at the slowest crack growth rates, near ΔK threshold, the presence of salt acts to decrease da/dN over that measured in air.

Galvanic Corrosion

When dissimilar metals are placed in an electrolyte and are electrically coupled, the possibility for accelerated corrosion, i.e. galvanic corrosion, exists. Preliminary design studies have identified Incoloy 800 as the leading alloy for high temperature containment and mild steel for use at lower temperature (<450°C). An experimental program was carried out to evaluate the galvanic corrosion of Incoloy 800 coupled to mild steel.

Using a potentiostat as a zero resistance ammeter, the galvanic potential and galvanic current established by a I800/C Steel couple when immersed drawsalt at 400°C were monitored as a function of of time. Mild steel was anodic relative to I800. The galvanic current and potential, see Figure 9, were very small and approached zero with time, indicative of a benign galvanic problem.

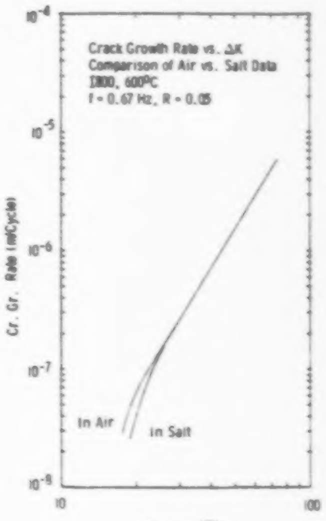

Figure 8. Crack growth rates for Incoloy 800 at 600°C in air and in drawsalt.

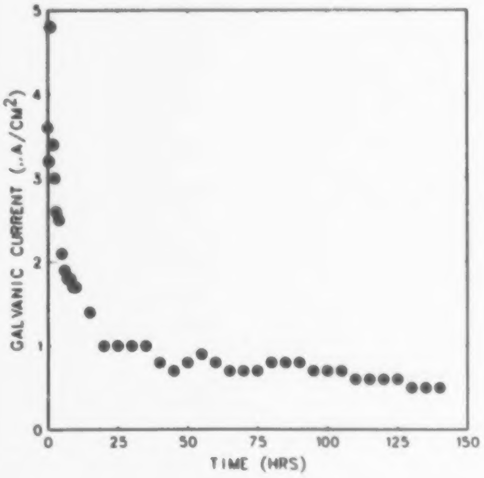

Figure 9. The galvanic current for the Incoloy 800/mild steel couple immersed in drawsalt at 400°C.

ACKNOWLEDGMENTS

In addition to the authors, the experimental program at Sandia Laboratories involves the following individuals: R. W. Bradshaw, D. A. Nissen and R. W. Carling. Their contributions to the preparation of this project summary are gratefully appreciated.

PROJECT SUMMARY

Project Title:	Molten Salt Thermal Energy Storage Subsystem Research Experiment
Principal Investigator:	Thomas R. Tracey
Organization:	Martin Marietta Denver Aerospace (Solar Energy Systems) P.O. Box 179 Denver, CO. 80201
Project Goals:	The primary program goals are to reduce the costs for molten salt thermal energy systems and to advance the state of the art in high temperature liquid containment. A prototype commercial thermal energy storage (TES) subsystem preliminary design rated at 1200 MWh_t is developed to define the requirements for an experimental program to resolve all problems. The experimental program consists of element to test to insure adequate life of critical elements and a subsystem research experiment (SRE) to demonstrate the entire system at a size adequate to resolve all technical problems.
Project Status:	The TES preliminary design is complete. It has a capacity of 1200 MWh_t and uses 839K (1050°F) molten nitrate salt in the internally insulated and lined hot tank and 561K (550°F) salt in the cold tank. The TES design was used to design the SRE which has a capacity of 7.0 MWh_t. The hot tank insulation system consisting of 0.35m (13.5 in:) of refractory brick with an Incoloy 800 waffled liner inside the carbon steel tank is the same in the SRE as in the TES. The external insulation is also the same. The SRE detailed design is complete. The carbon steel tanks for both the hot and cold tank are installed along with the pumps, gas fired heater, cooler, and piping. The internal insulation (refractory brick) for the inside of the hot tank is installed and the waffled liner is being installed. Elements of the liner have been fatique tested both at ambient and at operating temperatures. Also, a $1m^3$ test tank was built, loaded with 839K (1050°F) salt and pressurized to 3 bars (maximum expected hydrostatic pressure in the TES tank) for 19,000 cycles simulating a 30 year life. Testing of the SRE will start in November 1981 and extend through about April 1982. The testing will include tank change and discharge simulations and heat loss measurements. The data from the SRE and TES preliminary design will be used to update the TES preliminary design and cost estimates.
Contract Number:	20-2988
Contract Period:	November 1980 to April 1982
Funding Level:	$2,074,411
Funding Source:	Sandia National Laboratories - Livermore, CA.

MOLTEN SALT THERMAL ENERGY STORAGE SUBSYSTEM FOR SOLAR THERMAL CENTRAL RECEIVER PLANTS[1]

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ABSTRACT

The development of a low cost thermal energy storage subsystem for large solar plants is described. Molten nitrate salt is used as both the solar plant working fluid and the storage medium. The storage system consists of a specially designed hot tank to hold salt at a storage temperature of 839K (1050°F) and a separate carbon steel cold tank to hold the salt after its thermal energy has been extracted to generate steam. The hot tank is lined with insulating firebrick to reduce the shell temperature to 561K (550°F) so that a low-cost carbon steel shell can be used. The internal insulation is protected from the hot salt by a unique metal liner with orthogonal corrugations to allow for numerous cycles of thermal expansion and contraction. This paper describes a preliminary design for a large commercial-size plant (1200 MWh_t), a laboratory test program for the critical components, and the design, construction, and test of a small scale (7 MWh_t) research experiment at the Central Receiver Test Facility in Albuquerque, New Mexico.

INTRODUCTION

A wide variety of energy storage subsystems are currently being examined for use with large Solar Thermal Central Receiver (STCR) plants. One of the most attractive of such concepts is the use of a molten nitrate salt (60% $NaNO_3$, 40% KNO_3 by weight) as a sensible heat storage medium. This salt has low cost, high heat capacity per unit volume, low vapor pressure, and good heat transfer properties. Because the salt can also be used as the working fluid in the solar receiver, its use can considerably simplify the solar side of a plant; this enhances reliability and efficiency. The molten salt working temperature limits of approximately 561K (550°F) to 839K (1050°F) are ideally suited to the generation and use of high-pressure, superheated steam for either electrical power generation or industrial process heat applications. Of course, this storage concept can also be used with non-solar heat sources, such as fossil-fired salt heaters, with the same type of advantages.

Under the sponsorship of the Department of Energy and Sandia National Laboratories Livermore, we are conducting a Molten Salt Thermal Energy Storage Subsystem Research Experiment (SRE) program. The objectives of this program are to advance the state of the art in the high temperature containment of molten salt, to reduce the costs of thermal energy storage, and to resolve all uncertainties in this storage concept. Our approach is to contain the high temperature salt (839K/1050°F) in a lined and internally insulated hot tank, and to contain the cold salt (561K/550°F) in a separate tank made of carbon steel. The use of internal insulation allows the use of low-cost carbon steel as the shell material for the hot tank. The internal insulation is protected from the salt by a metal liner. The liner is a unique design employing a liquid-tight, waffled membrane of the type used extensively in liquid natural gas (LNG) storage applications. The internal insulation is a low-density insulating firebrick. The hot tank is also externally insulated to reduce heat losses to a minimum. The rest of the system consists of a cold tank (carbon steel with external insulation) and the necessary pumps, sumps, pipes, valves, and controls.

This program consists of the following key elements:

o Preliminary design and cost analysis of a 1200 MWh_t, commercial-size Thermal Energy Storage (TES) subsystem.

o A critical component development program for the liner and internal insulation; this includes numerous fatigue tests of both the liner and the brick, and culminates in the construction and fatigue testing of a laboratory prototype tank of one cubic meter volume with hot salt.

o Design, construction, and testing of a small-scale TES (7 MWh_t), termed a Subsystem Research Experiment (SRE). The SRE will consist of a hot tank, a cold tank, a fossil-fired heater to simulate a solar receiver, an air cooler to simulate a steam generator, and all pumps, sumps, controls, etc. necessary to simulate a complete system.

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[1] Work performed for DOE under Sandia Contract No. 20-2988 [2] Senior Staff Engineer [3] President

The SRE will be constructed at the Central Receiver Test Facility (CRTF) at Albuquerque, New Mexico. SRE testing will commence late in 1981. Development testing on the liner and internal insulation was completed in August 1981. The purpose of this paper is to give an overview of the work being performed on this program and the key results obtained to date.

COMMERCIAL STORAGE SYSTEM

A thermal energy storage (TES) subsystem of this general type consists of the following major components:

- Hot tank
- Hot sump and pump
- Cold tank
- Cold sump and pump
- Salt melter and reprocessor
- Associated piping and valves (heat-traced and insulated)
- Instrumentation and controls

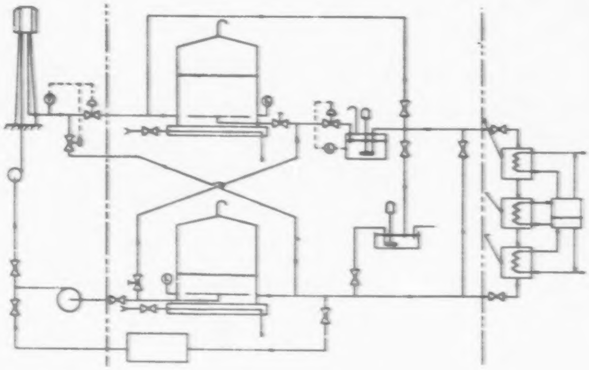

Figure 1 Solar Plant Schematic

In a solar plant, shown schematically in Figure 1, this type of TES would be used in the following way: Salt comes out of the solar receiver at 839K (1050°F) and flows directly into the hot tank. Once the hot tank has been partially filled, hot salt can be removed from it (via the hot sump and pump) and transported to the steam generator. The latter item is a separate subsystem from the TES. Salt leaving the steam generator is at 561K (550°F) and flows directly into the cold tank. Salt can then be taken from the cold tank and pumped up to the receiver on the top of the tower. Note that the solar receiver control strategy is based on controlling the salt outlet temperature by varying the flow rate through the receiver. Thus, the flow rate through the receiver will generally be different from that through the steam generator. This dual tank, sensible heat, thermal storage concept using a single liquid as the heat transfer medium (on both the input and output sides) and as the heat storage medium, has many advantages:

- Low cost due to use of molten nitrate salt and internally insulated hot tank with carbon steel shell.
- Simplified overall plant flow control with a minimum of components.
- Decoupling of steam generating rate from short-term fluctuation in solar insolation.
- Minimum thermal cycling on a specific tank, pump, pipe, etc., owing to use of dual tanks (especially as compared to a thermocline or cascade approach).

An important element in making this approach cost effective is the use of a lined and internally insulated hot tank. Consequently, the emphasis in this program is on the design, development, and testing of a hot tank with a service life of thirty years.

Figure 2 shows our design concept. The Technigaz liner design concept of a waffled metallic membrane was selected for this application because of its great success in cyrogenic LNG applications since 1964, and the fact that it was readily adaptable to this molten salt application. A picture of a typical LNG ship tank is shown in Figure 3, and a closeup of the LNG liner is shown in Figure 4. The orthogonal corrugations allow for repeated cycles of thermal expansion and contraction in both directions. The liner acts like a membrane in that it is liquid-tight but does not carry any pressure loads itself--rather, it transmits the loads through the internal insulation into the steel shell. The liner is designed to withstand the cyclic thermal expansion and pressure loads experienced over its thirty year life. Since in a solar plant operation the hot tank would be filled and drained at least once per day, fatigue effects are a major consideration in liner design.

Incoloy 800 was selected as the liner material bacause of its good strength, corrosion, and fatigue properties in this molten salt environment. This decision was based upon thousands of hours of material test data at 839K (1050°F) in molten salt generated under another solar energy program at Martin Marietta The liner thickness will be 1.27 mm (0.050 in.), as Incoloy 800 sheets of this thickness can be readily formed with corrugations, the predicted peak stress levels in service are acceptable, and it is close to the customary LNG value of 1.20 mm (0.047 in.) where there is a wealth of liner experience. It is important that the liner be liquid-tight over its service life. A leak would cause salt to flow into the internal insulation and ultimately to the steel shell. If uncorrected, this would obviously cause many problems such as over-temperature of the shell, shell corrosion, increased tank heat loss, permanent damage to the internal insulation, etc. The risk of potential leaks in the liner is reduced to the lowest possible level by leak testing every inch of every weld using an ammonia leak test method, and by extensive fatigue testing at (and above) realistic load levels. In addition, active leak detection methods will be used during solar plant operation so that if a leak should develop, the tank can be shut down and repaired. Personnel safety is provided by a dike around the tank.

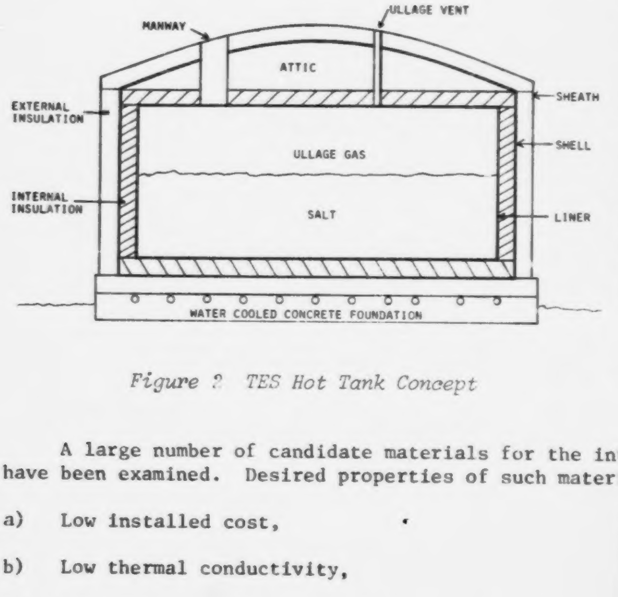

Figure 2 TES Hot Tank Concept

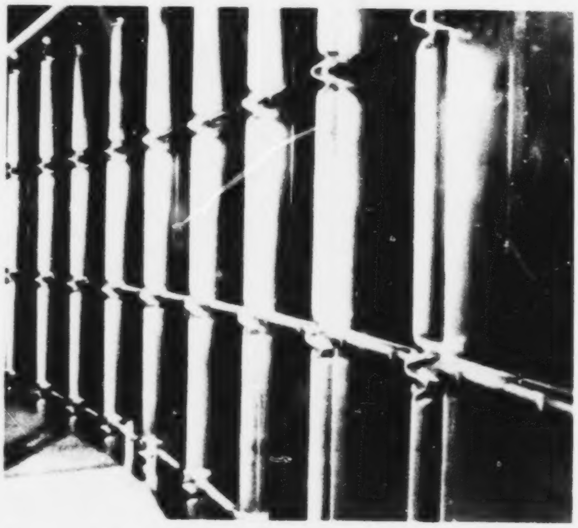

Figure 3 Inside of LNG Storage Tank Onboard Ship

A large number of candidate materials for the internal insulation used on the sidewalls and bottom have been examined. Desired properties of such materials are:

a) Low installed cost,

b) Low thermal conductivity,

c) Adequate strength at elevated temperatures,

d) Thirty-year service life,

e) Compatibility with molten salt for a period of several months in the unlikely event of a leak in the liner.

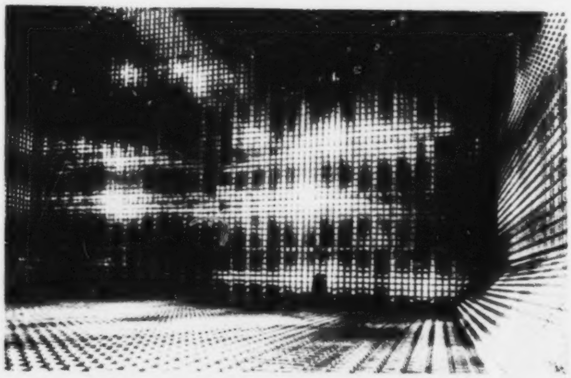

Figure 4 Closeup of Liner in LNG Land Storage Tank

Examination of these candidates considered such factors as installed cost per unit area, strength tests at elevated temperatures, and tests in molten salt. Based on this work, we selected Johns Manville C22ZSL insulating firebrick. Figure 5 shows the cost tradeoffs involved for this material for our hot tank application. The greater the brick thickness, the less the heat loss from the tank and, therefore, the less the cost of the solar collector system (principally heliostats) required to make up for the lost energy. Our shell temperature design criteria is 561K (550°F), and so the costs of the external insulation necessary to maintain this value are included in this figure. This design temperature was selected because it is below both the API and ASME code values, and because it results in a thermal expansion of the hot tank shell less than (or equal to) that of the cold tank shell.

It can be seen from Figure 5 that the brick thickness for minimum total cost is 0.389 m (15.3 in.). In view of the fact that brick only comes in discrete thicknesses, and that the total cost curve is so flat, we selected a design thickness of 0.343 m (13-½ in.). This allows the use of two layers of standard 9 x 4½ x 2½ in. size brick (extra large brick is also available in this thickness but at a cost premium). This brick has undergone extensive testing during this program, including over 4000 hours in molten salt, crush strength tests, creep tests, and fatigue tests, all conducted at 839K (1050°F). All of these test results indicate that this particular brick will be entirely satisfactory for this application. The brick will be installed using mortar and thermal expansion joints every few feet in both directions. Metal shelves will be used to support the brick on the vertical walls. On both the walls and the floor, the liner is attached to the steel shell with rods (called anchor pieces) which run through the brick. Thus, the liner, brick, and shell are intimately coupled both mechanically and thermally.

The internal insulation used on top of the hot tank is a common fibrous insulation. The hot tank also has external insulation, a board (or block) on the top, fibrous on the sides, and a castable on the bottom. The top and sides have weatherproof aluminum sheathing. The sheathing is painted white to reduce diurnal shell temperature variations due to the solar flux. Figure 2 also shows that the hot tank will sit on a water-cooled concrete foundation. Water-cooling was selected so as to ensure that the soil temperature was maintained at (or very near) ambient. This approach avoids the problem area of soil strength and stability at elevated temperatures for long periods of time.

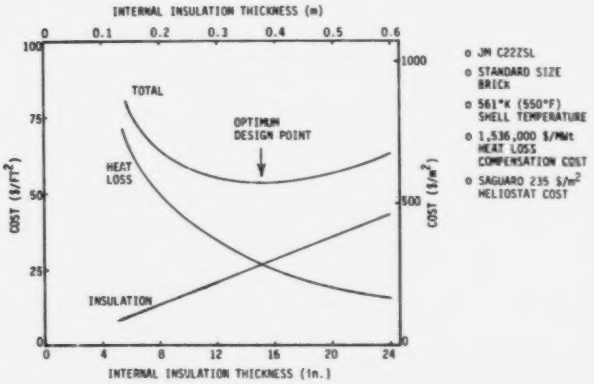

Figure 5 Optimized Insulation Design Methodology

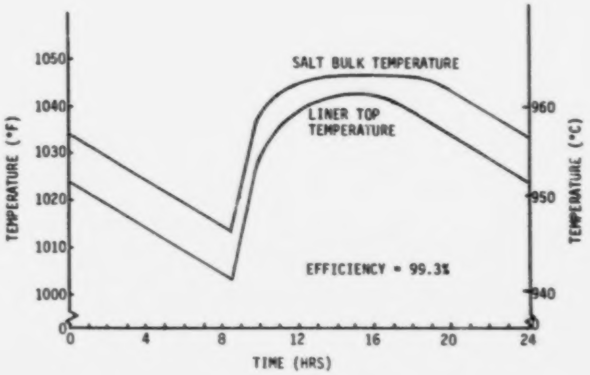

Figure 6 TES Hot Tank Temperature Predictions for Poor Solar Day

The tank shown in Figure 2 will store about 1200 MWh_t of thermal energy, enough to run a 120 MWe steam turbine-generator for approximately four hours. The liner inside diameter is 24.4 m (80 feet), and the inside height is 13.4 m (44 feet). In general, large storage tanks are more cost effective per unit energy stored than smaller ones owing to the reduced area-to-volume ratio. There are, of course, practical limits to how large a single tank can be. Maximum tank height is generally limited by the allowable soil-bearing strength, unless special foundations are used. We have used a typical value of 0.24 MPa (5000 psf) for this study. Tank height can also be limited by the ability of the liner to withstand the salt pressure; this is currently assessed at about 0.3 MPa (43.5 psi) which corresponds to a salt height of 17.7 m (58.1 ft). Maximum tank diameter is generally limited by the maximum permissible shell thickness without requiring post-weld treatment (3.8 cm/1.5 in. in the ASME code) for cost reasons.

This limits tank diameters to about 40-46 m (130-150 ft.). Cost optimization studies on the hot tank configuration (i.e., height-to-diameter ratio) show that for this 1200 MWh_t capacity, the tank height for precisely minimum cost is 24.5 m (80.3 ft.). However, these same studies also show that the cost curve is rather flat, and so the cost penalty for 13.4 m (44 ft.) height limitation is only about 3% of the total TES cost.

Figure 6 shows predicted values of the salt bulk temperature versus time for the 1200 MWh_t hot tank in one of many possible usage scenarios. In this particular scenario, the solar plant provides salt into the tank at a variable flow rate but constant temperature (839K/1050°F) between 8.5 and 15.5 hours, at which point the tank is full. The tank is then discharged at 300 MW_t for four hours until it is "empty." The tank is never completely empty in our design approach, since we would always leave a small residual in the tank overnight so as to reduce thermal cycling, avoid the possibility of getting air in the outlet pipes, and prevent freezing of the salt (494K/430°F) in case the sun does not shine for a while. The data of Figure 5 are based on a 0.41 m (16 in.) residual height, which is adequate to satisfy the above objectives (e.g., freezing would not occur for 2-3 weeks). It can be seen that the tank is well-insulated, and that the salt temperature stays high during the time of discharge (15.5 to 19.5 hours). Maximum heat loss rate for this hot tank is 0.38 MW_t, resulting in less than 0.8% of the maximum storage capacity being lost per day. The liner temperature is only about 3-6K (5-10°F) below the salt temperature due to the high radiative and convective heating rates at these temperatures.

DEVELOPMENT TESTING

A number of laboratory tests have been conducted on the liner and brick to ensure that they will function properly for the 30 year service life of this system. This research work was very important since Incoloy 800 had never before been used for a liner of this type, and since most previous liner applications have been cryogenic. Also, the JM insulating firebrick had not been used in this manner before. Liner testing began with the formation of 70 liner elements (i.e., small parts of one liner sheet) out of Incoloy 800 using commercial tooling. Knots (the intersection of two orthogonal corrugations) and angle pieces (small right angle pieces used at the corners of a tank) were easily formed and showed good dimensional control, although there was some slight "springback" effect. This was a major milestone in the program since there was some concern about formability with Incoloy 800 as its ductility is considerably lower than that of 304L stainless steel used in LNG applications.

A number of fatigue tests were then performed on these liner elements. The liner is subjected to two types of fatigue loading in service, salt pressure loads due to filling and draining the tank each day and thermal expansion loads. The latter consists of small amplitude diurnal temperature variations (e.g., Figure 5), larger amplitude (but longer frequency) temperature variations due to variations in the weather (such as storms, clouds, etc), and finally complete tank cooldown to ambient temperature for inspection and maintenance. These variations are difficult to quantify in general since they will depend upon solar plant specifics and weather behavior. For the purposes of this study, we have adopted the following design environments:

Fluid pressure: 0-0.3 MPa (43.5 psi) once per day for 30 years

Liner thermal expansion: 700-839K (800-1050°F) once per day for 30 years

The liner was tested in these fatigue environments in a series of tests of ever increasing realism. We began with a set of tests on the small elements described above. Six different kinds of tests were run:

1. Biaxial knot strain tests at room temperature.
2. Uniaxial angle piece strain tests at room temperature.
3. Knot pressure tests at room temperature.
4. Angle piece pressure tests at room temperature.
5. Biaxial knot strain tests at 839K (1050°F).
6. Uniaxial angle piece strain tests at 839K (1050°F).

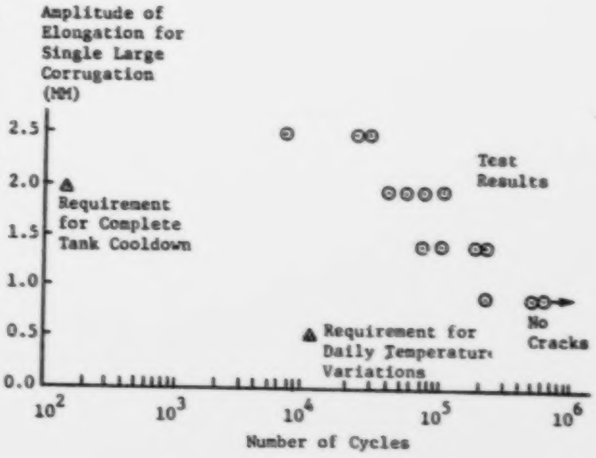

Figure 7 Knot Fatigue Test Results

Each of these strain tests involved 4 different load levels, and 3 or 4 specimens per level. The results of the strain tests on the knots are shown in Figure 7. It can be seen that the fatigue life of the knot is well above the required values. The elevated temperature strain tests gave essentially the same results. The pressure tests were all conducted at 0.3 MPa (43.5 psi) maximum load, and variations in manufacturing tolerances on the wall smoothness were simulated. It was found that there were no through cracks in any of the elements after 150,000 cycles of testing for reasonably smooth walls. An abrupt discontinuity of 2 and 4 mm under one of the feet of a knot reduced the fatigue life to 107,000 and 34,000 cycles respectively. This fatigue testing of liner elements has shown that the liner should withstand the design loads for a number of cycles that far exceeds the requirements for a hot tank at a solar plant.

Considerable testing was also done on the JM C22ZSL brick. This was necessary because even though this brick has been used for years in industry, no data were available on strength or fatigue life at at elevated temperatures. The results for testing in air can be summarized as follows:

o The average compression strength is 2.5 MPa (363 psi) with a standard deviation of 0.7 MPa (102 psi) at room temperature, and 2.4 MPa (348 psi) and 0.4 MPa (58 psi) at 839K (1050°F) respectively.

o There is no significant effect of direction, temperature or thermal cycles on compressive strength.

o The brick is undamaged after 145,000 cycles of compressive fatigue testing at applied load levels of 0-0.3 MPa (43.5 psi) or 0-.45 MPa (65.3 psi) at 839K (1050°F), and several samples have survived over 500,000 cycles.

o Brick at 839K (1050°F) has withstood a constant load of 1.0 MPa (150 psi) for 6 months without breaking.

Samples of this brick have also been immersed in molten salt at 839K (1050°F) for 6 months without any catastrophic damage due to chemical attack. These results give confidence that this brick is more than adequate to withstand the loads imposed in this application.

An important part of this development program is the construction and test of a small hot tank which was filled with 839K (1050°F) salt and subjected to cyclic pressure variations. This is called one cubic meter test since that is the interior volume of the tank. This tank was fabricated from large sheets of liner using anchor pieces and welded joints just like a large tank. It also used 0.34 m (13.5 in.) of JM brick, a carbon steel shell and external insulation like a large tank. The test setup and the test levels conformed to the ASME Code (Section III, Appendix II, Article II-1000) for experimental fatigue testing. The basic purpose of this test is to demonstrate that the liner and internal insulation will safely survive the TES environment for the desired service life. This is the only test in the program that will have full scale materials, dimensions, temperatures, pressures, and chemistry as well as a realistic number of pressure cycles.

The tank was exposed to 19,000 pressure cycles with an amplitude of 3 bars (58.1 ft. of salt) to simulate a 30 year fatigue life. At the conclusion of the test the tank was emptied and visually inspected using dye penetrant. There was no evidence of any cracks or leaks in the liner. Also, a section of the liner was removed and the brick was inspected. There was no damage to the brick and no salt leakage. The liner was repaired and leak checked to demonstrate repairability of the liner.

SUBSYSTEM RESEARCH EXPERIMENT (SRE)

The largest and most important element of this program is the construction and testing of a thermal energy storage system SRE at the CRTF in Albuquerque, New Mexico. The purpose of this effort is to demonstrate the fabrication techniques and performance characteristics of a lined and internally insulated hot tank, to demonstrate the operation of a complete storage subsystem, and to resolve all uncertainties in this design approach. A flow schematic for the SRE is shown in Figure 8. A 3 MW_t propane fired salt heater will simulate a solar receiver in heating the salt to 839K (1050°F) while a 5 MW_t fan driven air cooler will simulate the action of a steam generator. The SRE hot tank will have inside the liner dimensions of 3.06 m (10.04 ft.) diameter and 5.64 m (18' 6") height. This tank has a storage capacity of 7.0 MWh_t. These dimensions are sufficient to allow the use of full scale TES liner panels and insulation thicknesses in the tank construction. The SRE height and diameter are, of course, much smaller than the commercial size TES tank in order to keep the program within an R&D type budget. The height and diameter finally selected were a compromise between full scale simulation and budget considerations.

Construction of the SRE began in June 1981, and testing is expected to commence in the Fall of 1981. The design, construction, salt loading and system startup and checkout are being done using the same type of methods as would be used on a full scale commercial system. The testing will basically consist of performance testing and operational testing. In the former, we will measure the steady state heat loss of each tank at various salt levels and temperatures using electric heaters to maintain constant conditions. We will also measure the transient cooldown. These data will be used to confirm (and improve where necessary) analytical modeling procedures employed in system performance predictions. In the operational tests, utility operators will be employed to simulate how a TES subsystem would be used in the actual solar plants. This will involve daily charging and discharging of each tank. System safety, maintenance and repair procedures will also be demonstrated. It is expected that this storage SRE will be in operation for some time to come, and it is possible that someday it could be connected to a steam generator SRE and/or the molten salt receiver SRE.

As of the end of August 1981, the hot and cold tank shells and foundations have been installed along with the air cooler, gas fired heater, pumps and piping. The internal insulation is being installed in the hot tank and the liner installation will start in September. Other work remaining to be done includes installation of line and tank electrical heaters, installation of instrumentation and controls and the installation of external insulation in the tanks and lines. We plan to start system checkout in November 1981. A photograph of the SRE taken in July 1981 is shown in Figure 9. The hot tank is the higher one and the air cooler is shown in the background.

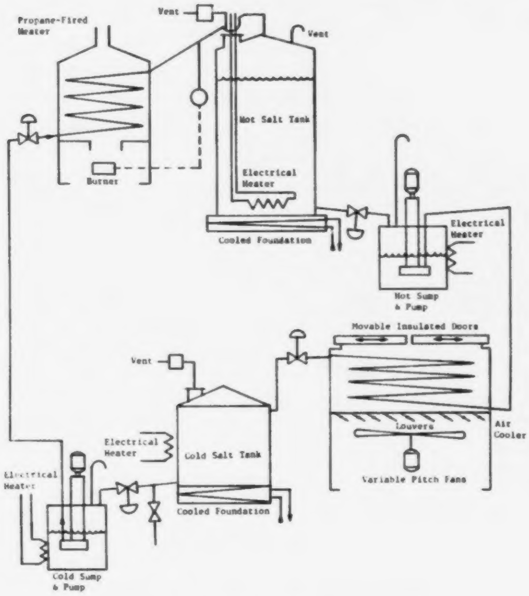

Figure 8 SRE Flow Schematic

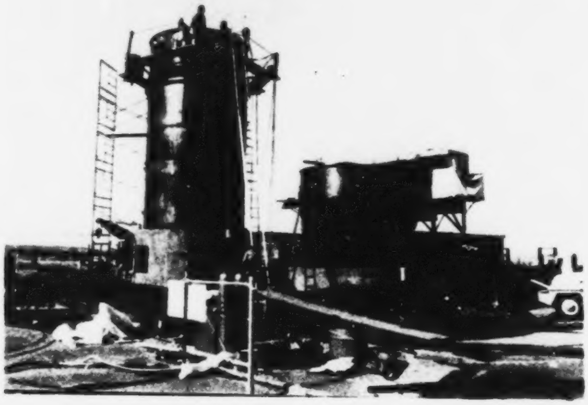

Figure 9 Photo of SRE - July 1981

CONCLUSIONS

An intensive development program is underway for a molten salt thermal energy storage system for solar plants. The use of a dual tank approach with a lined and internally insulated hot tank offers many possible advantages. Laboratory testing completed to date indicates that the Incoloy 800 waffled membrane liner and the insulating firebrick insulation are more than strong enought to withstand the loads in a commercial tank for a 30 year service life. Construction is prodeeding on a complete storage system SRE at the CRTF in Albuquerque, New Mexico. Testing is planned to start in November 1981.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the important contributions made to this work by Mr. Tom Tracey, Mr. Owen Scott and Mr. Charles Bolton at Martin Marietta, Mr. Ted Conlon at American Technigaz Inc., Mr. Charles Zermati and staff at Technigaz S.A., Mr. Bob Williamson and staff at Stearns-Roger, and Mr. Eric Weber of Arizona Public Service Co.

PROJECT SUMMARY

Project Title: Thermal Conductivity of Molten Alkali Nitrates

Principal Investigator: Harald Øye

Senior Researcher: Bjørn Hafskjold

Organization: Institute of Inorganic Chemistry,
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Project Goals: Experimental determination of the thermal conductivity of mixtures of $NaNO_3$ and KNO_3 in the temperature range 350-600°C. Study of the effect of small additions of CO_2 and H_2O. Development of a theoretical model for the thermal conductivity.

Project Satus: Literature survey and method evaluation has been completed. Hardware has been constructed and electrical systems tested. Test experiments have been made on water at room temperature and data analyses have been made.

Future work consists of testing an optical temperature detection system, test and production experiments, data reduction and modelling.

Contract Number: SANDIA 20-2992

Contract Period: September 1, 1980 - June 30, 1982

Funding Level: $ 100,000

Funding Source: U.S. Department of Energy through Sandia National Laboratory.

THERMAL CONDUCTIVITY OF MOLTEN ALKALI NITRATES

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ABSTRACT

A method for simultaneous determination of the thermal conductivity and thermal diffusivity of fluids has been evaluated. The method is based on the transient heat conduction following a step-wise heat generation in a strip of metal foil immersed in the fluid. It is an absolute method in the sense that no calibration constant is involved. Equipment has been built capable of measuring molten nitrates in their stable liquid temperature range under a controlled atmosphere. Test experiments have been made on water.

INTRODUCTION

Heat transportation in molten salts can be a combination of conduction, convection and radiation. The design of equipment where heat exchange is a concern will depend on knowledge of the three mechanisms separately. In particular, the DOE program for Thermal Energy Storage for Solar Thermal Applications requires a set of physical properties of molten alkali nitrates for the design of heat exchangers and storage tanks. Our contribution to this will be the experimental determination of the thermal conductivity and thermal diffusivity in mixtures of $NaNO_3$ and KNO_3 at 350 - 360°C.

The thermal conductivity, k, is defined by Fourier's law

$$J_q = - k \cdot \nabla T \tag{1}$$

where J_q is the heat flux, that is the amount of heat conducted per unit time and unit area, and ∇T is the temperature gradient. Fourier's law can be transformed to the heat equation

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T \tag{2}$$

where $\partial T/\partial t$ is the time derivative of the temperature, and ∇^2 is the Laplace operator. The thermal diffusivity κ is related to k by

$$\kappa = k/\rho \cdot c_p \tag{3}$$

where ρ is the density and c_p the heat capacity of the fluid.

An experimental determination of k and κ is based on Eq. (1) or (2) in differential or integrated form. Both equations involve a thermometric, a distance, and a time measurement, whereas Eq. (1) involves an additional calorimetric measurement. Boundary conditions that relate the equations to the geometry of the equipment and the experimental procedure complete the formal basis for the measurements.

In this paper we discuss the chosen method, the integrated form of Eq. (2), and its application to molten alkali nitrates. The equipment is described. Test experiments on water and data analyses are discussed.

METHOD EVALUATION

Steady state [1-3] as well as transient [4,5] methods have been applied to molten nitrates. Transient methods are clearly better suited to meet our requirements of being absolute, fast, and accurate. Additional requirements are simple hardware construction, two independent temperature detection systems for consistency checks, minimum contact between liquid and temperature probe, and elimination of convection and radiation.

We have chosen the so-called "hot-strip" method developed by Gustafsson *et al.*[4] The essential feature of our design is the heating element, a metal foil about 10 cm long, 3 mm wide and 50 μm thick immersed in the fluid. Heat is generated electrically at a constant rate, starting from an equilibrium situation at zero time. The solution of Eq. (2) contains parameters specific for the geometry of the apparatus and the fluid being measured and no reference fluid is necessary for calibration. The "hot-strip" is similar to the "hot-wire", but has the advatage of higher surface-to-volume ratio, which improves the thermal contact between metal and fluid.

Each measurement takes less than ten seconds, which is fast enough to avoid convection. Radiation is eliminated by employing a small temperature increase, i.e. 1-2°C, in the heating element.

The temperature detection systems are based on the resistance of the metal strip and the refractive index of the fluid. Both properties are temperature dependent for the materials in consideration. The resistance is determined from a recording of the potential drop along the foil, and the refractive index from an interferometric analysis of laser light passing through the sample.

THEORY

The heating element is shown schematically in Fig. 1, which defines the coordinates used in the following. Assuming that the effect of finite length in z-direction is negligible, the solution of Eq. (2) will be independent of z. The boundary conditions are

$$T = T_o \quad \text{at } t = 0 \tag{4}$$

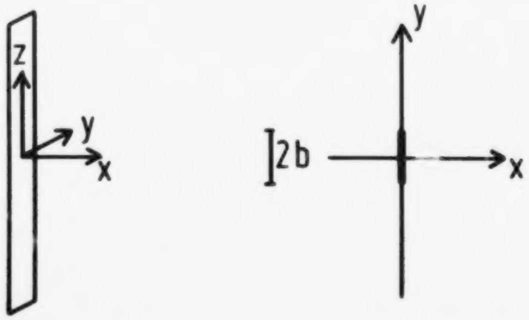

Figure 1. Geometry of the heating element

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and

$$\lim_{\substack{x \to \infty \\ y \to \infty}} T = T_o \, , \qquad (5)$$

which lead to the integrated form of Eq. 2[4]

$$T(x,y,t) - T_o = \frac{q}{4k\,\pi^{\frac{1}{2}}} \int_o^{2(\kappa t)^{\frac{1}{2}}} d\sigma \exp(-x^2/\sigma^2) \left[\mathrm{erfc}\left(\frac{y-b}{\sigma}\right) - \mathrm{erfc}\left(\frac{y+b}{\sigma}\right) \right] \qquad (6)$$

Here, q is the heat production rate per unit area of the foil and erfc(u) is the Error function complement

$$\mathrm{erfc}(u) = \frac{2}{\pi^{\frac{1}{2}}} \int_u^{\infty} e^{-x^2} dx \qquad (7)$$

Implicit in Eq. (6) is the assumption that the foil is of zero thickness and heat capacity. With Eq. (6), k and κ can be determined from a recording of $T - T_o$ at given x,y, and t when q and b are known. The determination of $T - T_o$ will be made indirectly through the resistance of the foil and the optical properties of the fluid.

The resistance R of the foil at x = 0 is given by

$$R/R_o = 1 + \frac{\alpha}{2b} \int_{-b}^{b} \left[T(0,y,t) - T_o \right] dy \qquad (8)$$

where R_o is resistance at $T = T_o$ and α is the thermal coefficient of the resistance. Evaluation of the integral leads to[4]

$$R/R_o = 1 + \frac{\alpha q}{2k\,\pi^{\frac{1}{2}}} \left[\tau\, \mathrm{erf}(2b/\tau) - \frac{\tau^2}{4b\,\pi^{\frac{1}{2}}} (1 - e^{-4b^2/\tau^2}) + \frac{b}{\pi^{\frac{1}{2}}} E_1 (4b^2/\tau^2) \right] \qquad (9)$$

where $\tau = 2(\kappa t)^{\frac{1}{2}}$ and

$$E_1 (u) = \int_u^{\infty} x^{-1} e^{-x} dx \qquad (10)$$

For small τ, *i.e.* $\tau/b \ll 1$, a good approximation to Eq. (9) is given by

$$R/R_o = 1 + \frac{\alpha q}{2k\,\pi^{\frac{1}{2}}} \left(\tau - \frac{\tau^2}{4b\,\pi^{\frac{1}{2}}} \right) \qquad (11)$$

The difference in optical distance travelled by two light beams in y-direction, one at a distance x from the foil and the other sufficiently far from the foil to experience no temperature increase is

$$\Delta(x,t) = \frac{\partial n}{\partial T} \int \left[T\,(x,y,t) - T_o \right] dy \qquad (12)$$

Here ∂n/∂t is the thermal coefficient of the fluid's refractive index. Computation of this integral must be done numerically, but the analysis is otherwise similar to that described above.

MATERIAL TESTS

The (optical cell) salt container is made of quarts, which has been found resistant to the nitrates in dry atmosphere.

The heating element must, in addition to being chemically stable, also be electically protected in order to avoid current leak through the melt. Two concepts have been tested; protecting the metal with insulating coatings based on boron nitride and a ceramic material, and using metals that form protective oxide layers. The coatings did not adhere well under varying thermal conditions and were also attaced by the melt. Aluminum was tested with and without anodizing and is in both cases protected by its oxide layer. Tantalum is presently tested out and will probably be the chosen material, as it appears to behave similar to Al and has better mechanical properties.

EQUIPMENT

A survey photo of the equipment is shown in Fig. 2

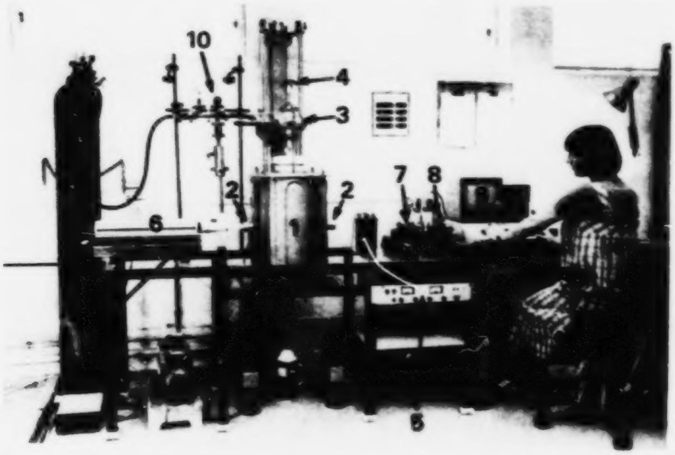

Figure 2. Thermal conductivity apparatus.

The furnace (1) with optical windows (2) contains the cell with salt and heating element. Cell support (3) and electrical terminals (4) are located at the top of the furnace. DC current is supplied by a HP 6263 power supply (5), and the voltage over the foil is recorded by a HP 3456A digital voltmeter (not shown). Light for the optical temperature detection system is supplied by a Spectra Physics 120 He-Ne laser (6) and analyzed by a variable shearing interferometer (7) and linear photodetector (8). The experiment is run from an Apple II computer (9), which also logs and processes the data. Vacuum and gas supply is connected (10).

TEST EXPERIMENT

Using a heating element made of ordinary household aluminum foil, a test of the electrical system has been made in water at room temperature. The foil width was 2.9 mm. The heating current was 3.0054 A, which gave a heat production of 2176 $W \cdot m^{-2}$. The voltage drop over the foil was recorded as function of time at 40 readings per second, and the result is shown in Fig. 3. It should be emphasized that this test experiment was not undertaken with accurate determintations of κ and k in mind, but rather to illustrate the method and data analysis.

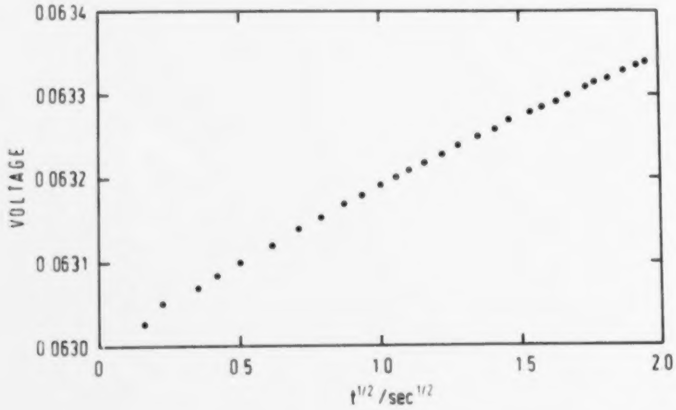

Figure 3. Measured voltage over foil as function of square root of time.

The optical temperature detection system has not yet been implemented.

DATA ANALYSIS

A second-order polynomial in $t^{\frac{1}{2}}$ was fitted to the measured voltage

$$U = U_o + U_1\, t^{\frac{1}{2}} + U_2 t \qquad (13)$$

The standard deviation in the fit was 0.002%. This indicates the measurement system's capability of obtaining the projected goal; *vis.* accurate determinations of thermal conductivity and thermal diffusivity. Rater than associating the coefficients U_1 and U_2 with the corresponding terms of Eq. (11), it was decided to determine κ from the time derivative of $r = R/R_o = U/U_o$;

$$\dot{r} = \partial r/\partial t = \frac{\alpha q}{\rho c_p \pi^{\frac{1}{2}}} \left[\frac{1}{\tau}\, \mathrm{erf}\left(\frac{2b}{\tau}\right) - \frac{1}{2b\pi^{\frac{1}{2}}} \left(1 - e^{-4b^2/\tau^2}\right) \right] \qquad (14)$$

From Eq. (2), it is seen that $\dot{r}$ is the natural quantity for a determination of κ. From a set of values for τ, $\dot{r}$ was computed according to Eq. (14) and inserted into the expression for experimental times derived from Eq. (13);

$$t = \frac{1}{4} \left(\frac{U_1}{U_o}\right)^2 \left(\dot{r} - \frac{U_2}{U_o}\right)^{-2} \qquad (15)$$

The thermal diffusivity was then obtained as the slope of $\tau^2/4$ versus t, as follows from the definition of τ. This gave for water $\kappa = 1.7 \cdot 10^{-7}$ m^2 s^{-1}, using the literature values[6] $\alpha = 42.9 \cdot 10^{-4}$ k^{-1}, $\rho = 998$ kg $\cdot$ m^{-3} and $c_p = 4182$ J $\cdot$ $kg^{-1}K^{-1}$. The literature value for κ is $1.47 \cdot 10^{-7}$ m^2s^{-1}.[6]

With the value for κ determined, the bracket in Eq. (9) can be computed at the experimental times. A plot of r *versus* these computed values can then be used to determine k. This gave k = 0,63$Wm^{-1}K^{-1}$ as compared to the literature value 0.60$Wm^{-1}K^{-1}$.[6]

PROJECT STATUS

We are in the middle of the project and are not able to report results at the present time. Apparatus building and testing have taken somewhat longer time than anticipated. Several designs and ideas have been tried before reaching the present set-up.

The mathematical tools including computerization have been worked out. The experimental technique based upon measuring resistance in heated foil appears to work well. Aluminum and tantalum are both found to be satisfactory materials for the foil. The high-temperature system is in operation and has been tested.

The preliminary experiments, which were performed without concern about high accuracy, have given results for k and κ in fair agreement with literature values for water.

We have now received precision-cut foil of aluminum and tantalum and test experiment with water and production experiments on nitrate melts will be started in August, 1981. Parallel with this work the optical systems will be further developed. The results are,however,not dependent on the development of the optical method as the present method based on measuring the resistance in the foil yields all the information required for determination of k and κ. We do,however,consider it very advantageous to determine the heat transport parameters by two different methods. Finally we expect to model the data.

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ADDENDUM: THERMAL CONDUCTIVITY OF MOLTEN ALKALI NITRATES

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As a result of recent progress, we can now report the first values for the termal conductivity k and thermal diffusivity κ for water and molten $NaNO_3$. The results were obtained as described in our paper[1], using a Ta foil of precise dimensions, in test experiments summarized in Table 1.

Table 1. Test results for k and κ for water and molten $NaNO_3$. Equation numbers refer to our paper[1] and numbers in parenthesis are literature references.

System	T/°C	$\kappa \times 10^7/m^2s^{-1}$		$k/Wm^{-1}K^{-1}$		
		Eqs. 14 and 15	literature value	Eq. 9	Eq. 3	literature value
Distilled water	20	1.43	1.41 at 18.5°C	0.581	0.599	0.592 at 17°C 0.609 at 27°C (3)
"	20.3	1.40	1.44 at 22.5°C (2)	0.573	0.584	
"	20.1	1.38				
$NaNO_3$	315	$1.59^{a)}$	1.69 at 310°C, 1.70 at 343°C (4)	$0.524^{a)}$	$0.545^{a)}$	0.51-0.59 at 315°C (fig.3 of ref 4)
"	"	$1.64^{b)}$		$0.531^{b)}$	$0.554^{b)}$	
"	"	$1.83^{c)}$	1.62 at 315°C (5)	$0.526^{c)}$	$0.568^{c)}$	

a) Based on $c_p = 1821.4\ Jkg^{-1}\ K^{-1}$ (from ref. 6)
b) Based on $C^p = 1794.9\ Jkg^{-1}\ K^{-1}$ (from ref. 4)
c) Based on $C_p = 1647.2\ Jkg^{-1}\ K^{-1}$ (from ref. 7)

We have concluded from these results that our present implementation of the method described in ref. 1 is accurate to within 3 per cent for water in both k and κ, and probably within the uncertainties of literature values for $NaNO_3$, again in both quantities. For $NaNO_3$, we have used three different literature values for C_p[4,6,7], which give a significant variation in κ but not in k. The consistency in k as obtained from eqs (9) and (3) is better than 3.1 per cent for water and better than 4.3% for $NaNO_3$ except the last entry, for which the two results for k differ by about 8 per cent.

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PROJECT SUMMARY

Project Title: Corrosion Behavior of Alloys

Principal Investigator: Robert A. Osteryoung

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Project Goals: The objective of this work is to study the chemistry of solutes in molten sodium-potassium nitrates at temperatures in the 250-550°C range and to obtain information which will permit an understanding of the corrosion behavior of structural alloys that will be employed in thermal loops in solar power systems. Studies related for formation of passivating films on pure metals, such as iron and nickel, as well as Incoloy 800, will be carried out.

Project Status: Initial work involved studies of glassy carbon (abandoned as too restrictive), platinum and gold as indicator electrodes for solute study in molten nitrates. Platinum appeared to have a wider and more reproducible potential range for the study of solute in the nitrate melts at 550°C. Open circuit potentials and polarization curves for iron, nickel and Incoloy 800 were obtained at up to 550°C. From the shape of the current-potential curves and examination of the electrode, it was concluded that Incoloy 800 undergoes more extensive pitting and crevice corrosion at 250 than 550°C, perhaps the result of a more adherent and dense passive oxide film forming at the higher temperature.

Contract Number: 20-4478

Contract Period: May 5, 1980 - March 31, 1982

Funding Level: $85,100

Funding Source:
Sandia Laboratories
Livermore, CA 94550

CORROSION BEHAVIOR OF ALLOYS

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ABSTRACT

The electrochemical behavior of glassy carbon (G.C.), platinum, gold, iron, nickel and Incoloy 800 (I800) electrodes in molten $(Na,K)NO_3$ has been investigated over a wide range of temperatures. While G.C. has been found unsuitable for electrochemical studies of solubles species in this melt, Pt and Au show good behavior even at the highest temperature reached (550°C) although Pt appears somewhat better. Anodic polarization curves as well as open circuit potential measurements for Fe, Ni and I800 show evidence of spontaneous passivation when these metals are in contact with the melt at any temperature studied. Pitting and crevice corrosion has been found in I800 at potentials more anodic than the steady-state potential, this phenomenon being more important at the lowest temperature investigated (250°C), than at the highest (550°C).

INTRODUCTION

As part of the effort in the development of molten $(Na,K)NO_3$ salts as heat transfer fluids in solar collectors at temperatures in the vicinity of 550°C, studies of the corrosion behavior of potential container materials are quite important.(1) Although corrosion of Fe, Ni, some steels and to a lesser extent Cr has been studied in molten nitrates(2-4) most of these studies involve temperatures well under 550°C and the results are not directly applicable to high temperature, molten salt solar collector systems. Incoloy 800 (I800) has been proposed as a suitable container material for molten nitrates at elevated temperatures and the results of relatively long term corrosion studies have recently been published.(5) In the work reported here, we initially were interested in studying the behavior of soluble metal ions which might be derived from the corrosion of structural alloys in the molten binary $(Na,K)NO_3$ system at temperatures up to 550°C. Our initial efforts involved studies of glassy carbon, platinum and gold as indicator electrodes in these melts and the corrosion behavior of Fe, Ni and I800 at elevated temperatures.

EXPERIMENTAL

The electrochemical cell was made either of pyrex (experiments with G.C. electrode) or quartz (for the rest of the metals) following conventional design. The $(Na,K)NO_3$ was contained in a gold crucible and purified in the usual manner.(6) G.C. rod was sealed into pyrex tubes, showing a disc surface of 0.07 cm^2. Pt, Au, Fe and Ni were wires of different diameters, all of 99.9% purity or higher. I800 electrodes were either cylindrical or square cross section rods made from commercial samples supplied by Sandia. All electrodes were polished with emery paper and finally with 0.3 µm alumina powder on a polishing cloth. The counter electrode was a Pt spiral placed in a separated fritted compartment. The reference electrode was a Ag/Ag^+ (0.08 m $AgNO_3$) for the experiments with G.C., while either the gold crucible or a gold wire dipped in the same melt or a gold foil in a separate fritted compartment acted as "quasi" reference electrode for the rest of the metals. Any contact between glass tubes and the melt was minimized by use of gold foil sleeves. A gold-deposited quartz furnace was used and the temperature was controlled with a thermocouple probe connected to a temperature controller. The experiments with G.C. were performed under purified Ar atmosphere; the remainder of the experiments were performed under an O_2 atmosphere.

G.C., Pt and Au Electrodes

Electrode studies were performed on G.C. to 350°C, and up to 550°C on Pt and Au. Cathodic runs show similar characteristics for this group of electrodes up to 350°C. A well defined cathodic peak is observed at around -1.55 V vs the gold reference electrode, due to the electroreduction of nitrate ion and formation of a passivating film.(8) The variation of peak potential and peak current with the sweep rate is typical of that expected for a precipitation-dissolution process under ohmic control.(7) As the temperature increases, the cathodic limit is shifted to more anodic potentials,

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around -0.55 V and -0.40 V on Pt and Au, respectively, at 550°C. The experimental activation energies are 11 and 9 Kcal/mol for Pt and Au, respectively, for the cathodic peak. Upon reversing the cathodic run after the NO_3^- reduction peak is obtained, an anodic peak at around -0.9 V vs gold for the oxidation of the passivating film is observed for the three electrodes. This peak decreases with increasing temperature, probably due to the higher solubility of the oxide film with temperature. Another smaller anodic peak appears at more anodic potentials (which disappear as the temperature increases) around -0.5 V on Pt and Au, and -0.35 V on G.C. This peak, according to Zambonin,(8) is due to the oxidation of O_2^- ion. Anodic runs on Pt and Au show quite similar characteristics, but are different on G.C. For Pt and Au the reversible peaks for the NO_2^-/NO_2 couple are well defined at lower temperatures (250-350°C) but for temperatures above 350°C the anodic oxidation peak of NO_2^- overlaps the NO_3^- oxidation and is no longer observable; the overvoltage for the oxidation of NO_3^- is lowered as the temperature increases. For both electrodes, the anodic limit at 550°C is around +0.50 V. For G.C. the anodic limit overlaps the oxidation wave of NO_2^- even at the lowest temperature and shifts to more cathodic potentials as the temperature increases, inhibiting any electrochemical study of soluble species at the temperature of interest (550°C).

Fe, Ni and I800 Electrodes

Open Circuit Potential (OCP) - Time Curves: The OCP shifts to more positive potentials with time immediately after immersion for all the temperatures examined, indicating that the electrodes became passivated when in contact with the melt. The higher the temperature the shorter the time taken to reach steady-state potentials and the more noble (positive) the steady-state values. The passivating films are mainly Fe_3O_4 and NiO for iron and nickel,(2) respectively, and an outer film of Fe_3O_4 and an intermediate mixed oxide spinel $(Fe,Cr)_3O_4$ for I800.(5) In the presence of $CrO_4^{=}$ ion, steady-state potentials for I800 tend to be slightly less noble than in the pure melt. The initial OCP of a previously passivated I800 electrode is about the same as its original steady-state value, suggesting that the passivating film is strongly attached to the electrode surface.

Current-potential Curves: Anodic polarization curves were carried out at a scan rate of 0.2 mv/sec for all the metals, unless otherwise noted. All anodic polarization experiments were initiated after the electrodes had reached their steady-state open circuit potentials, and covered the 250-550°C temperature range for Fe and I800 and 350-550°C for Ni. The curves are characterized by an initial increase of anodic current at potentials near the OCP; the current then continues to increase much more slowly with subsequent increase in potential. At more anodic potentials (around +0.5 V for the lowest temperature) NO_2^- ion oxidation takes place and a limiting current is established in the case of Fe (Fig. 1) and I800 (Fig. 2). As the potential is made more anodic, a sudden increase in current is found. No limiting current for NO_2^- oxidation was observed for Ni electrodes; instead the current increases very rapidly at around +0.6 V for lower temperature experiments and around +0.9 V for the high temerature (550°C) experiments (Fig. 3). The E/log i characteristics show the same features mentioned above at all temperatures investigated. The higher the temperature the higher the currents on the initial part of the E/log i curves as well as on the limiting oxidation current plateau of NO_2^- (in the case of Fe and I800). Typical active-passive transitions were not found in any case, probably the result of the spontaneous passivation of the metal surfaces when in contact with the melt. That is, the melt itself is a highly effective oxidant which results in a passive layer being formed on Fe, Ni and I800.(2,9) Thus, at the start of the polarization experiments the electrode surface is already covered by a passivating oxide film. Passive currents for I800 are lower than for Fe and Ni. Experimental activation energies in the passive region are 26, 25 and 21 Kcal/mol for Fe, Ni and I800, respectively. I800 suffers pitting and crevice corrosion following anodic polarization current-potential scans, giving $Cr_2O_7^{=}$ ion as a soluble product in the melt at lower temperatures. This corrosion phenomenon is much more pronounced at the lower temperatures (250°C), as evidenced by a large closed current loop in the E/log i curve (Fig. 4) and by visual observation of the electrode surface. The surface oxide film is apparently stronger and more protective at higher temperatures but susceptibility to pitting corrosion, as can be inferred from E/log i curves (Fig. 4), and from observation of the electrode surface. The presence of small amount of $CrO_4^{=}$ ion (0.01 M) in the melt slightly increases the passive current but apparently diminishes the susceptibility to pitting corrosion (Fig. 5).

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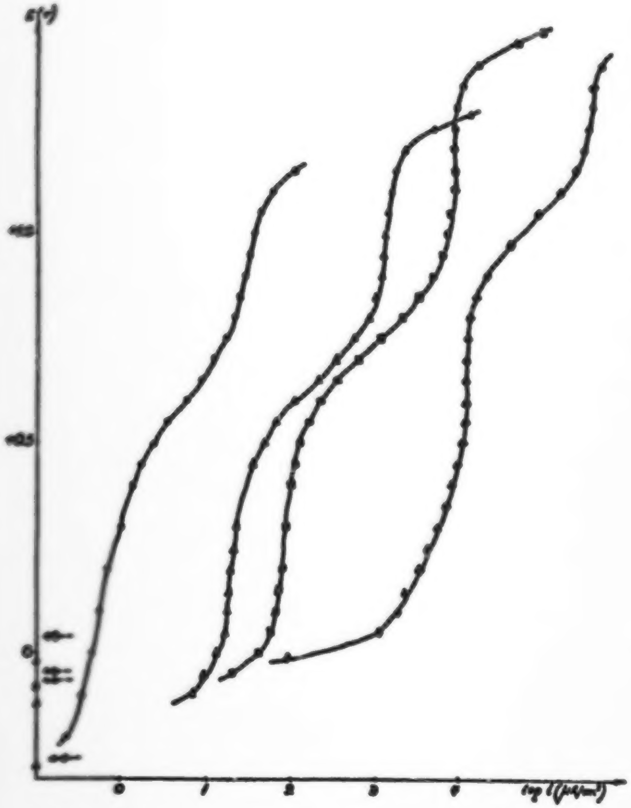

Figure 1. E-log i anodic polarization curves for iron in molten nitrate system at different temperatures; (o) 258, (▲) 345, (□) 398, (◇) 548°C, ν = 0.2 mV/sec. On each curve, horizontal arrows indicate the rest potential (OCP) attained after the experiment was completed.

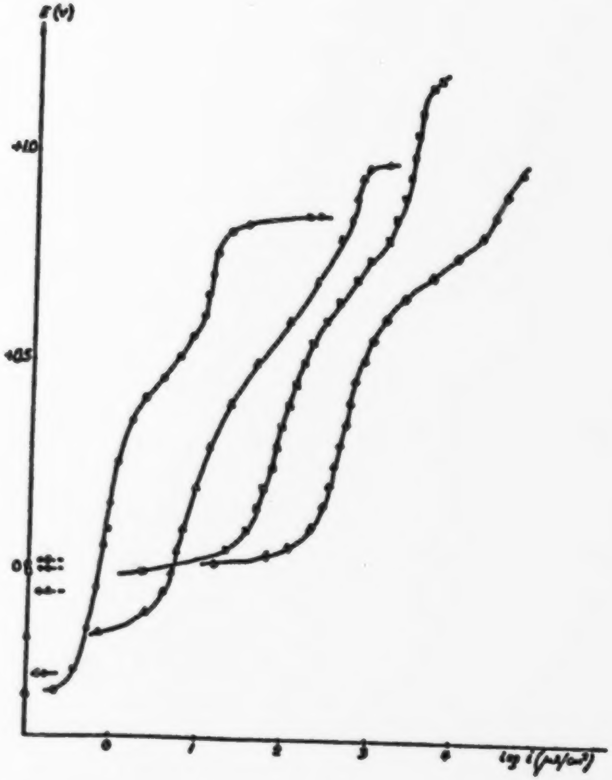

Figure 2. E-log i anodic polarization curves for Incoloy 800 alloy in molten nitrate system at different temperatures: (o) 250, (▲) 357, (□) 453, (◇) 547°C, ν = 0.2 mV/sec. On each curve horizontal arrow indicates the rest potential attained after the experiment was completed.

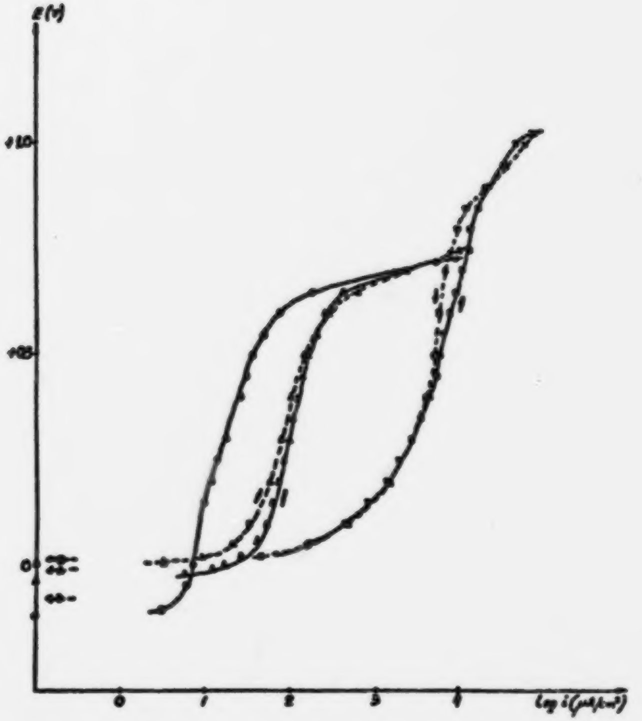

Figure 3. E-log i anodic polarization curves for nickel in molten nitrate system at different temperatures: (o) 345, (Δ) 398, (□) 548°C, ν = 0.2 mV/sec. Dotted lines represent the reverse scan and horizontal arrows the rest potentials.

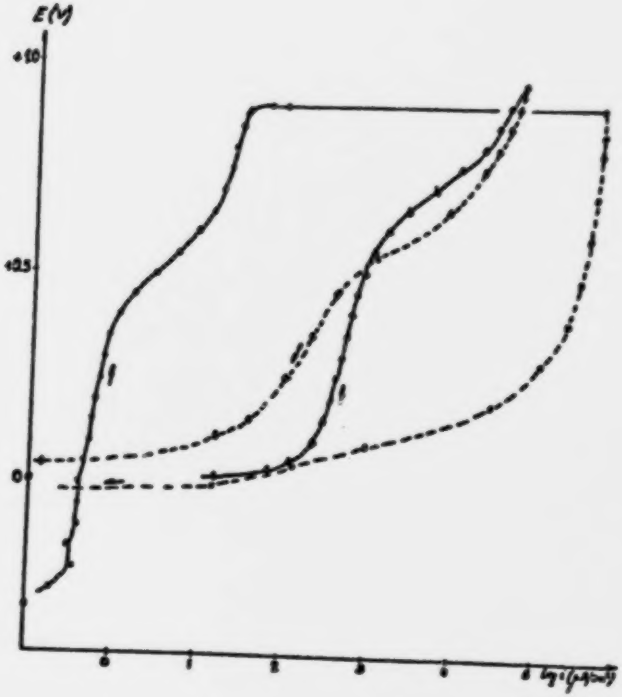

Figure 4. Cyclic E-log i polarization curves for Incoloy 800 alloy in molten nitrate system. (o) T = 250°C; forward scan rate 0.1 mV/sec; reverse scan rate 5 mV/sec; (◊) T = 547°C; forward and reverse scan rate 0.2 mV/sec.

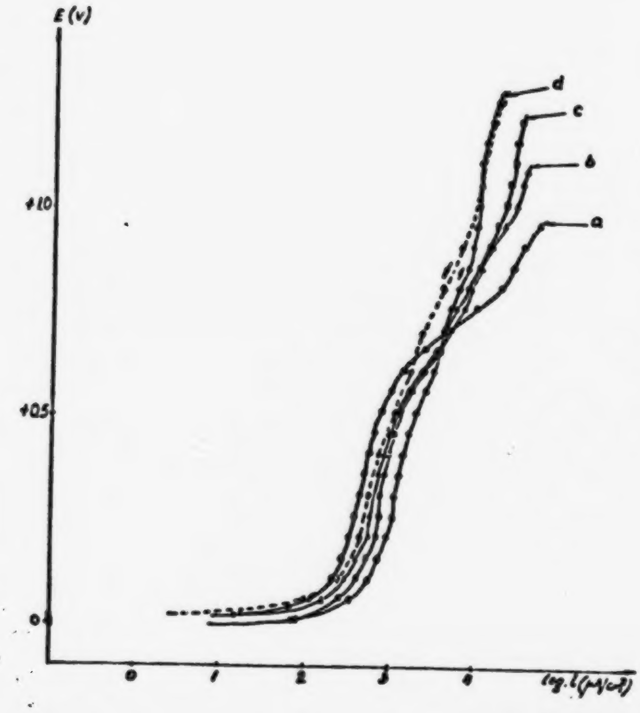

Figure 5. E-log i anodic polarization curves for Incoloy 800 alloy in molten nitrate system at different concentrations of added K_2CrO_4: (○) pure melt, (△) 0.001, (□) 0.006, (◇) 0.010 M, T = 547°C, ν = 0.2 mV/sec. Dotted line represents reverse scan.

PROJECT SUMMARY

Project Title: Effects on Soils from Hot Storage Tanks

Principal Investigator: Kenneth C. Ko

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Project Goals: Develop an understanding of the soils data and analyses needed to establish the technical feasibility of underground and on-ground hot storage tanks.

Project Status: The project to date is at the mid-point of the investigation. Also methods of soil treatment are being studied at this time.

Based on the distribution of the soil elements in the Continental U.S., two representative soil models have been developed. Each element in the soils was studied for their physical, chemical and mechanical behavior at elevated temperatures up to 1500°F (816°C). The behavioral parameters were integrated to analyze the gross changes in the soil properties.

Environmental effects of the spillage of heat storage media into the soil foundation was studied. The effects were analyzed for four storage media and two soil models at four different operating temperature ranges.

Based on the results of the investigation, a set of remedial foundation treatment methods will be presented, relative feasibility of each method, and a set of recommendations for further research will be developed in the area of laboratory and field soils behavior.

Contract Number: SNLL 84-1171

Contract Period: April 20, 1981 through October 19, 1981

Funding Level: 69,891

Funding Source: U.S. Department of Energy through Sandia National Laboratories, Livermore (SNLL)

EFFECTS ON SOILS FROM HOT STORAGE TANKS

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ABSTRACT

Behavioral characteristics of foundation soils for hot storage tanks have been investigated on two soil models representative of the soils in the Continental U.S. The changes in the engineering properties of the foundation soils due to heating and the effects of four storage media liquids; hydrocarbon oil, silicon oil, molten nitrate salt and liquid sodium into the foundation have been investigated. The remedial measures such as soil preconditioning to alleviate the detrimental effects of the heat on soils will be presented and the areas for further research will be delineated.

INTRODUCTION

The use of liquid and/or solid storage media contained within tanks at high temperature has been proposed as an economically viable method of a back up system for solar thermal power systems. The thermal storage tanks are designed as to contain the following storage media:

1. Hydrocarbon oil at temperatures up to 316°C (600°F)
2. Hydrocarbon oil and rock at temperatures up to 316°C (600°F)
3. Silicon oil at temperatures up to 399°C (750°F)
4. Molten nitrate salt at temperatures up to 566°C (1050°F)
5. Liquid sodium at temperatures up to 593°C (1100°F)
6. Refractory brick at temperatures up to 816°C (1500°F)

Potential problems exist due to the changes in the properties of foundation soils at the high temperature levels. These changes are both physical and chemical, including dehydration, and decomposition. Decomposition of the soil minerals may cause the emission of carbon oxides and sulphur oxides depending on the chemical composition of the soil elements.

The decomposition of soil elements and emission of gases will result in the lessening of mechanical strength and decrease in the physical volume of the soil. The hot tank could eventually settle further into the ground. Depending on the soil strata, such settlement can be non-uniform. The differential settlement will cause local stress concentration on the tank structure, especially that of underground, which may fracture the tank. Should the tank fail, the effects of the leakage of the contained high temperature liquids must be considered.

COMPOSITION OF SOILS NEAR THE SURFACE

The distribution of soil and rock materials near the surface and down to a depth of 30 meters of the continental crust have been estimated from various publications with consideration of varying geologic composition are listed in Table 1, (ref. 1, 2). The figures include an estimation that in 20% of the continental area, the metamorphic, plutonic and volcanic rocks are weathered deeply enough to be considered as clay soils. The soil materials in each of these areas can be related to the parent rocks as given in the table.

The characteristics of two soil models can be selected from the distribution table presented below; a moderately favorable condition and a moderately unfavorable condition. The contrasts between these two will serve to define the critical properties and outline the steps needed to assess the suitability of specific sites. The two models are defined in Table 2.

Table 1. Distribution of Surface Earth Materials

	Percent of total continental surface area
Sand and gravel	16%
Clay and shale	41%
Carbonates (limestone, dolomite)	15%
Evaporites (salt, gypsum, anhydrite, potash)	1%
Volcanic rocks (rhyolite-basalt series)	11%
Plutonic rocks (granite-gabbro series, peridotite)	7%
Metamorphic rocks*	9%
Other (phosphate, coal, peat, ores)	much less than 1%
	100%

*includes gneiss, schist, slate amphibolite, but not marble. Marble is included with carbonates.

Table 2. Composition of Two Soil Models

Components	Content by weight	
	Model A	Model B
Quartz	40%	10%
Feldspar	40	20
Amphibole (hornblende)	5	5
Pyroxene (augite)	5	5
Micas (muscovite and/or biotite)	2	6
Expansible clays (montmorillonite group)	< 5	20
Stable clays (kaolinite and illite groups)	< 5	25
Gypsum and caliche (carbonates)	0	6
Organics	< 2	< 2
Soluble salts	< 1	< 1
Sulfides	< 1	< 1

Models containing amounts of organic constituents (soil humus or other organic decomposition products) are not considered because these normally are restricted to the upper one meter of surface soil. It is assumed that this material would be removed in preparation of the tank storage site. The comparatively rare instances of deep organic soils, such as bog soils or coal beds near the surface, are also excluded.

Model A represents the favorable foundation soil and consists of relatively pure sand and gravel (including arkoses) made up mainly of quartz, feldspars, and minor amphibole and/or pyroxene.

Model B is representative of a relatively poor, but common, type of foundation condition for this application. It is a soil with major amounts of clay minerals, varying amounts of salt, gypsum ($CaSO_4 \cdot 2H_2O$), plus carbonates and bicarbonates of calcium, magnesium, and sodium. By a conventional method of soil classification used in foundation engineering, the two models can be represented by grain size distribution curves as shown in Figure 1.

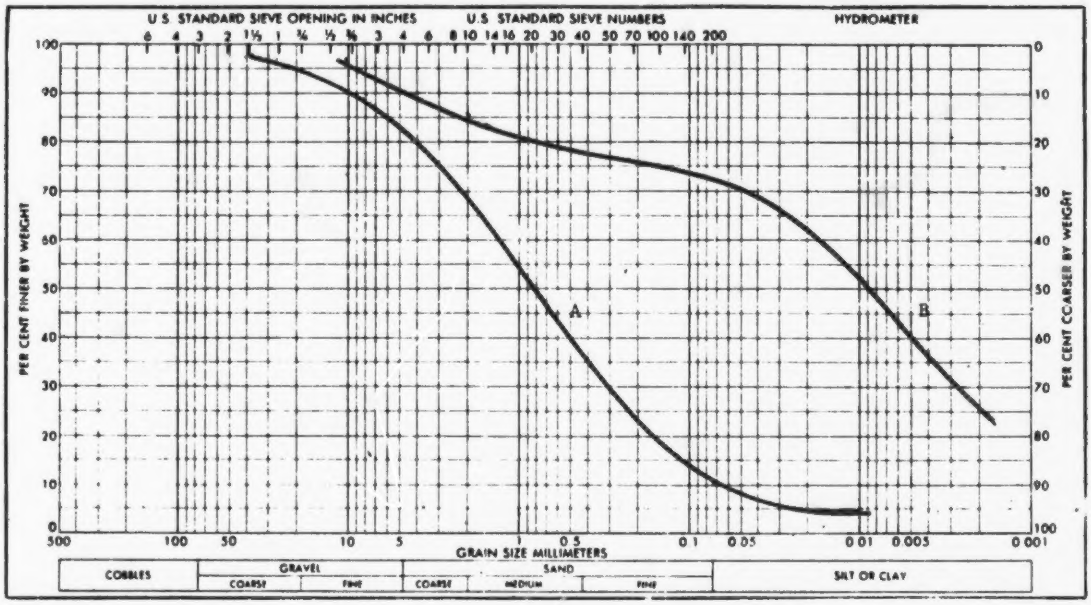

Figure 1. Soils Composition by Texture

CHANGES IN SOILS PROPERTIES DUE TO HEATING

The changes in soils and rocks that result from heating can be categorized as follows:

1. Polymorphic transitions (solid state reactions)
2. Dissociation reactions:
   Dehydration
   Decarbonation
   Desulfurization
3. Melting reactions:
   Anhydrous melting
   Melting under water

Each of these processes will be considered, with respect to the upper 30 meters of surface material. The confining pressure will be taken to be in the range from one to two atmospheres.

The materials in Model A soils have melting temperatures well above 1000°C. In these materials the temperature range to 816°C is below that needed to produce melting or decomposition. The important changes in this model are phase changes (polymorphic transitions), thermal expansion, and dehydration.

In the case of model B, dehydration of the clay minerals will occur on any significant heating above ambient temperature. The most important dehydration steps are in the temperature ranges of 100-200°C and 450-600°C. In the lower temperature range, the loosely held water of hydration will be driven off, resulting in a reduction in volume. Also in the lower temperature range, the interstitial water will be evaporated. However, thermal expansion of the mineral grains will partially compensate for the loss of water. The net expansion or contraction cannot be predicted at this point.

The soil components listed in Table 2 can be categorized into four primary mineral groups,---silicates, carbonates, sulfides and clays. The elements within a group behave similarly and therefore it is more convenient to study the components in each group as a unit. The properties of each mineral group is discussed in the following.

SILICATES: There are at least nine different crystallographic forms (polymorphs) of silica, all having the composition SiO_2. Six of these are common enough to be significant in the present study. These have the mineral names quartz, tridymite, and cristobalite. Each of these has a low temperature (alpha) form and a high temperature (beta) form, to make up the six common crystallographic forms of silica. The only reaction that may be expected at the temperatures under study will be the breakdown and rearrangement of the crystalline form at the atomic level. Generally most of the silicates are extremely stable at high temperatures for they were initially formed at extremely high temperatures. Feldspars generally show no change or alteration until 900°C except pure albite which exhibits a slight endothermic reaction at 820°C. The amphiboles may be expected to undergo polymorphic transformation, recrystallization or some to become anhydrous after 800°C (ref. 3). It appears pyroxenes may behave similar to that of the amphiboles but no detailed study has been located as of this time. Most of the micas will undergo reactions similar to those of clay and therefore should be examined with the clays.

CARBONATES: The common carbonate minerals are the carbonates of calcium, iron, and a mixture of calcium and magnesium. The minerals are as follows:

		Crystal System
Calcite	$CaCO_3$	Hexagonal (Rhombic)
Aragonite	$CaCO_3$	Orthorhombic
Dolomite	$CaMg(CO_3)_2$	Hexagonal (Rhombic)
Siderite	$FeCO_3$	Hexagonal (Rhombic)

Calcite and aragonite have the same composition, but differ in crystal form and therefore differ in other properties. Calcite decomposes at 900°C (at P = 1-2 atm), so it can be considered inert in the temperature range of this investigation. However, calcite is slightly soluble in water, and more soluble in hot water than in cold. The less common form of $CaCO_3$, aragonite, is not stable at near-surface temperatures and pressures but it can exist metastably. Aragonite is a high-pressure and low-temperature form of calcite and is always metastable at conditions prevailing near the surface of the earth. However, the transition from aragonite to calcite under these conditions is so slow that aragonite can exist metastably for geologic periods of time. On heating, aragonite changes to calcite at 520°C.

Dolomite decomposes at about 600-700°C, with release of carbon dioxide (CO_2). At low pressures the CO_2 will be evolved as a gas, and at higher pressures will go into solution in the water.

The decomposition of siderite starts at about 500°C, and is a complex reaction. The endothermic decomposition, yielding FeO and CO_2, is normally followed by an exothermic reaction as the FeO oxidizes to Fe_2O_3. The sequence takes place at the range of 500-650°C.

SULFIDES: The commonest sulfide minerals in soils are pyrite and marcasite, the two crystallographic forms of FeS_2. Other forms of iron sulfide, having the approximate composition of FeS, also occur and can be important in some cases. Other sulfides such as those of zinc, lead, copper, and many other metals are much less common. The common sulfides decompose on heating, at about 400-600°C when dry. They decompose at much lower temperatures under hydrous, oxidizing conditions. The sulfides liberate SO_2 gas under oxidizing conditions, and other oxides and/or sulfuric acid under hydrous conditions. These sulfur compounds, if present in significant amounts, are powerful agents for taking other soil materials into solution. In addition, the sulfurous gases are toxic to animals and man and would present a safety hazard. Damage to vegetation could also result in areas down-slope from the storage site. At present it appears that any significant amounts of sulfides in the soil (more than about 1%) would render the site unsuitable unless placed above ground with air circulation beneath it. Many of the reactions are much different in dry conditions than when estimated with water. For example, the dehydration of the common iron oxide occurs at 370°C when dry, but at 130°C when saturated with water at 1-2 atmospheres. The common sulfides of iron decompose at 400-600°C when dry, but at much lower temperatures when saturated with oxygenated water.

CLAY: There are primarily five clay minerals that make up the bulk of clay mineralogy; kaolinite, halloysite, smectite (montmorillonite) illite and chlorite. Of these it should be noted that only illite contains a non-expandable lattice structure with the addition of water. The clays are highly reactive with an increase in temperature yielding volumetric changes, as during expansion and contraction, and the breakup of the weakly bonded water resulting finally as an entirely new mineral. It has been observed that the clay minerals undergoes volumetric changes generally not in a straight forward expansion or contraction but instead through various phases or stages of expansion or contraction to contraction or expansion and then a possible final reversal. From previous studies examined to date kaolinite shows a slight expansion up to 500°C then contraction, halloysite has a similar reaction. Illite illustrated a more pronounced expansion up to 800°C then either a) a devastating collapse or b) a drop to the original size then followed by reexpansion. Meanwhile the smectites might show no change whatsoever up to 400°C then contract as with beidellite var smectite or may contract immediately then go into expansion at 200°C with a reversal at 800°C montmorillonite (bentonite) var smectite (ref. 4).

Through the use of differential thermal curves one may determine at what temperature ranges a) the breakdown of the weak bonded institual water molecules b) the breakup of the hydroxyl radical and c) the alteration into a entirely new compound, mineral. Kaolinite generally has one endothermic reaction occurring between 600-700°C with the entire breakup of institual water and hydroxyl at relatively the same moment followed between 900-1000°C by an exothermic reaction that may yield mullite and γ-alumina, at higher temperatures cristobalite will form. Similar reactions were observed with halloysite. Illite showed a considerable loss of water below 100-150°C, the initial endothermic reaction. At 450-550°C a secondary endothermic reaction began, peaking out in the vicinity of 550-650°C and a final endothermic reaction between 850-950°C. The exothermic reaction at 900-1000°C yields a composite structure of amorphous glass and spinel. Two endothermic reactions are usually exhibited with the smectites specifically montmorillonite and these usually occur between 100-200°C and 600-700°C. An exothermic reaction exists between 900-1000°C yielding a variety of minerals at varying temperatures such as spinel, mullite, cristobalite and cordierite (ref. 3,4).

Additional research is necessary to understand the effects of rehydration and redehydration, the interreaction of clay minerals at high temperatures and specific range of values for expansion and contraction.

ENVIRONMENTAL EFFECTS

Environmental effects without spillage is thought to be minimal. Assuming that there is adequate fencing, etc. the effect on the ambient environment should be small. The temperature discussed here will preclude the growing of plants in the general vicinity and may kill some birds if insulation cannot keep the surface heat down, but mammals should possess sufficient ability to stay away. One problem could be a general increase in ambient heat levels if these tanks were numerous in a community of houses which would create a need for greater air conditioning capacity in homes. This latter is a question which needs to be addressed since cities are well known for their temperature 'bubbles'. With all the concrete and asphalt in a city temperatures within, say, Denver are hotter than outside and cooling takes longer during the evening. This can be helped by the use of plantings but, as pointed out above, the high temperature of these tanks will preclude vegetation.

Spillage of the tank contents from leaks or massive failures is the environmental effect one would most generally associate with these hot tanks. Such environmental effects of spillage would depend on whether the tank is above ground, below ground in some sort of chamber which can contain the spill, or below ground simply buried in the soil material. Information gathered to date suggests that any tank put underground should be either in a chamber that can contain the spill, or have the soil so treated (cement grout) that it will contain the leak. In general, environmental effects of the spill may not be very significant but clean-up of such a spill from a buried tank may be next to impossible.

The areas which need further investigation are:

1. Possible soil/oil reactions and movement in soil.
2. Solubility of minerals in nitrate solution.

Nitrates are known to be good solvents of inorganic materials and it is therefore possible to assume that they will dissolve some of the soil minerals. The nitrates would also produce serious problems if they should enter our drinking water which is regulated by EPA for public health. Sodium would also present similar problems.

REMAINING PROGRAM

The main question remaining is: What is the possibility of a leak or massive failure? The failure of a tank will be mainly due to the differential movements of foundation soils at the high temperature levels. The foundation movements would be exhibited by the sum of the changes in the individual mineral properties. The question which naturally precipitates from this is: Can the soil material properties be controlled to reduce the possibility of the tank failures? These are the questions to be answered by the remaining program of the project.

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PROJECT SUMMARY

Project Title: Selection and Conceptual Design of an Advanced Thermal Energy Storage Subsystem for Commercial Scale (100 MWe) Solar Central Receiver Power Plant

Principal Investigators:
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Donald C. Schluderberg
Thomas P. Suchocki

Organization:
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Project Goals: Develop a thermal energy storage system that offers cost/performance advantages over the oil/rock thermocline concept selected for the Barstow Pilot Plant and that would be applicable to solar-repowered electric generating plants.

Project Status: Phase I, Selection and Conceptual Design, has been completed and the results reported in SAND-80-8190 (BAW-1662, Feb. 1981).

A conceptual design was developed for an advanced thermal energy storage system which is applicable to a 100 MWe solar central receiver plant using water/steam as the working fluid. Operating conditions studied were 510C/10.1 MPa (950F/1465 psia) from the receiver and 299C/2.72 MPa (570F/395 psia) from storage. The concept offers potential for cost and performance improvements over the oil/rock thermocline concept presently being installed at the central receiver 10 MWe pilot plant under construction in Barstow, California. The Moving Bed Thermal Energy Storage System (MBTESS) uses a free-flowing refractory material as the heat transport and storage media.

A conceptual design was developed for the MBTESS, including estimates for cost and performance, which utilizes helical screw lift conveyors to transport sand into heat exchangers mounted on top of cold and hot storage tanks. Assessment of the design for application to higher storage temperatures likely with molten salt or sodium receivers was made. A breakdown of power and storage related energy costs for both Barstow conditions and higher temperature conditions was developed to support the conclusion that a thermal energy storage concept can be developed which is capable of operation over a wide range of temperatures for all major receiver working fluids.

Technical issues in the MBTESS design were identified and programs of laboratory subscale experiments recommended for resolution. In addition, a development plan was prepared for a subsystem research experiment leading to a commercial scale design.

Contract Number: Sandia National Laboratories No. 20-2990A

Contract Period: September 1, 1980, through March 31, 1981

Funding Level: $157,283

Funding Source: U.S. Department of Energy through Sandia National Laboratories - Livermore

CONCEPTUAL DESIGN OF THE MOVING BED THERMAL ENERGY STORAGE SYSTEM FOR A COMMERCIAL SCALE (100 MWe) SOLAR CENTRAL RECEIVER POWER PLANT

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ABSTRACT

A conceptual design was developed for an advanced thermal energy storage system which is applicable to a 100 MWe solar central receiver plant using water/steam as the working fluid. Operating conditions studied were 510C/10.1 MPa (950F/1465 psia) from the receiver and 299C/2.72 MPa (570F/395 psia) from storage. The concept offers potential for cost and performance improvements over the oil/rock concept presently being installed at the central receiver 10 MWe pilot plant under construction in Barstow, California. The Moving Bed Thermal Energy Storage System (MBTESS) uses a free-flowing refractory material as the heat transport and storage media. The study included estimates for cost and performance, and suggestions were made for further development work leading to full-scale implementation of the concept.

INTRODUCTION

The development of economical and reliable thermal energy storage is considered a necessity for the successful commercialization of solar thermal power stations. A solar central receiver pilot plant (10 MWe) is being constructed at Barstow, California. The Thermal Energy Storage Subsystem (TESS) for this plant is an oil/rock dual-media storage system. As lead laboratory for Thermal Energy Storage for Solar Thermal Applications (TESSTA) program, Sandia National Laboratories Livermore initiated a development program to produce an advanced TESS offering cost/performance advantages over the oil/rock concept. The development program is divided into three phases.

This paper describes the results of the Phase I work performed under Sandia Contract No. 20-2990A for identification and conceptual design of an advanced TESS. The work was accomplished during the period from September, 1980, to February, 1981, and reported in Reference 1. The objectives of Phase I were to identify a concept that has cost and performance advantages over the oil/rock concept of Solar One and to develop a commercial-scale (100 MWe) conceptual design supported by budgetary cost estimates.

If authorized, Phases II and III will include the activities necessary for successful operation of a commercial- scale advanced storage subsystem meeting the established cost and performance goals.

EVALUATION: SELECTION OF ADVANCED THERMAL ENERGY STORAGE CONCEPTS

The study included the following scope of work:

- Select a preferred advanced thermal energy storage concept.
- Prepare a design and budgetary cost estimate for a commercial-scale system.
- Assess the design with respect to potential improvements and limitations.
- Assess the design with respect to higher temperature operation.
- Prepare a plan for construction and testing of a subsystem research experiment in Phase II.
- Outline a development plan and schedule for a commercial-scale subsystem.

The following concepts were considered as advanced TESS candidates:

- Caloria/granite - thermocline
- Moving sand bed - hot/cold tanks
- Air/rock - thermocline
- Molten salts - hot/cold tanks
- Pressurized hot water - underground hot tanks
- Sodium - hot/cold tanks
- Syltherm 800^R / taconite - trickle thermocline

BEST DOCUMENT AVAILABLE

System requirement specifications were provided for design and performance parameters.[2] The receiver working fluid conditions and the storage discharge steam conditions specified were those of a 100-MWe, commercial central receiver solar thermal power plant system[3], which the Barstow 10-MWe Pilot Plant represents. These values were as follows:

Extractable storage capacity, MWht	1710
Charging level, MWt	260
Discharging level, MWt	285
Discharge Duration, hours	6
Storage tank operating pressure	Atmospheric
Receiver outlet temperature, C (F)	510 (950)
Receiver outlet pressure, MPa (psia)	10.1 (1465)
Storage outlet temperature, C (F)	299 (570)
Storage outlet pressure, MPa (psia)	2.72 (395)

The concepts were initially screened by analyzing their characteristics, including the following:

- Energy storage density
- Media and containment materials
- Thermal efficiency
- Structural considerations
- Maintenance requirements
- Storage medium deterioration/replacement

Engineering judgment was applied to compensate for a scarcity of conceptual design information for the performance conditions specified. The number of concepts for further evaluation was reduced to four. They were:

- Air/rock thermocline using air as the heat transport medium and a rock bed as the thermal storage medium.
- Moving sand bed using a fine, free-flowing refractory powder as both heat transport and storage media.
- Molten salt sensible heat using a HITEC^R salt (40% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3 by weight) as the heat transport and storage fluid.
- Oil/rock thermocline using a Caloria oil as the heat transport fluid and granite as the storage medium.

Conceptual designs were prepared for each concept based on the system requirement specifications, including system schematics, subsystem mass balances, temperatures and heat exchanger and storage media parameters. Costs were compared for selected major system equipment (heat exchangers, storage tanks, pumps/lifts, and thermal storage medium). Selection criteria were developed based on the system requirement specifications and the project objectives:

- Equipment costs
- Round-trip efficiency
- Availability/reliability/maintenance
- Development requirements and risks
- Environmental and safety aspects
- Applicability to higher temperatures

The likelihood of improvements from further optimizations was also considered. The evaluation showed the oil/rock thermocline concept to be the lowest cost option at the Barstow temperature/pressure conditions. However, the 332C (630F) temperature limitation of the Caloria (heat transport fluid) precludes its application to higher temperature operation. The air/rock concept appeared to involve slightly lower capital costs than the moving sand bed or molten salt concepts, but the air/rock round-trip efficiency was about 15% lower because of the requirement to drive air circulating fans. As a result, the moving sand bed and molten salt concepts provided lower evaluated costs than the air/rock concept.

The moving sand bed concept was found to have slightly lower capital and operating costs than the molten salt concept. Additionally, the moving sand bed is capable of operation at storage temperatures above the maximum working temperature and below the freezing temperature of molten salts. It was also concluded that the cost of the moving sand bed concept could be further reduced by optimization of the number of tanks and lengths of the lifts. Therefore, the moving sand bed concept was selected for further conceptual design development.

CONCEPTUAL DESIGN OF THE MOVING BED TESS (MBTESS)

The subsystem and its component designs were directed toward an optimum combination of low equipment cost, minimum R&D requirements, operating flexibility, and round-trip efficiency. In the design evaluation, three configurations were produced, the third of which became the basis for the reference arrangement of the conceptual design and the one considered to be an optimized combination of tanks, lifts, and heat exchanges.

Optimization of this concept reduced the number of system components and costs of major equipment by \$11 million. The number of tanks was reduced from 18 to 12; the number of lifts, from 36 to 12. The calculated round-trip efficiency was improved from 68.9 to 70% due to reduced lift power requirements. As shown in Figure 1, the optimized design provides two cold and two hot hopper-type storage bins connected by helical screw lift conveyors, where the outer casing and helical screw rotate as an assembly. The charge and discharge heat exchangers are mounted atop the storage bins for easy access. The particulate material (sand) is also the heat transport medium. Sand flows by gravity over the heat exchanger surface at a low velocity. Special design features, such as inclined tubes, an inclined shell, and the tube arrangement, prevent material stagnation and provide a high sand bed density throughout the heat exchangers for maximum heat transfer. The basic design characteristics of the moving bed thermal energy storage system design are given below.

Storage Medium

Material	SiO_2
Operating range, C (F)	204-332 (400-630)
Density, kg/m^3 (lb/ft^3)	1522 (95)
Specific heat, J/kg-^{o}F)	1030 (0.246)
Particle size, 10^{-3} mm (10^{-4} in.)	44-74 (17-29)
Void fraction	0.40
SiO_2 mass, 10^8 kg (10^8 lb)	1.33 (2.94)

Tanks

No. of storage tanks	4
Volume per tank, 10^4 m^3 (10^5 ft^3)	1.02 (3.60)
Total volume, 10^4 m^3 (10^6 ft^3)	4.08 (1.44)
Material	ASTM A-53 (carbon steel)
Design temperature, C (F)	343 (650)
Insulation material, internal	
Sides and bottom, mm (in.)	SiO_2, 457.2 (18)
Roof	Thermal Wool II, 114.3 (4.5)

Heat Exchangers

	Discharge	Charge
Number	6	6
Duty, MWt (10^8 Btu/h)	47.5 (1.62)	43.4 (1.48)
Design flow		
Tube side (W/S), 10^4 kg/h (10^5 lb/h)	6.85 (1.51)	4.05 (8.92)
Shell side (SiO_2), 10^6 kg/h (10^6 lb/h)	1.45 (3.19)	7.94 (1.75)
Surface area, m^2 (ft^2)	819 (8820)	1124 (12,100)
Tube OD, mm (in.)	19 (0.75)	19 (0.75)
Material	Carbon moly	Carbon moly

Lifts

Number	12
Length	56.7 (186)
Outside diameter, m (ft)	1.95 (6.4)
Material	Carbon steel
Lift angle	35°
Capacity/lift, m^3/s (ft^3/s)	0.036 (12.7)
Horsepower/lift, hp	800
Lift speed, rpm	29

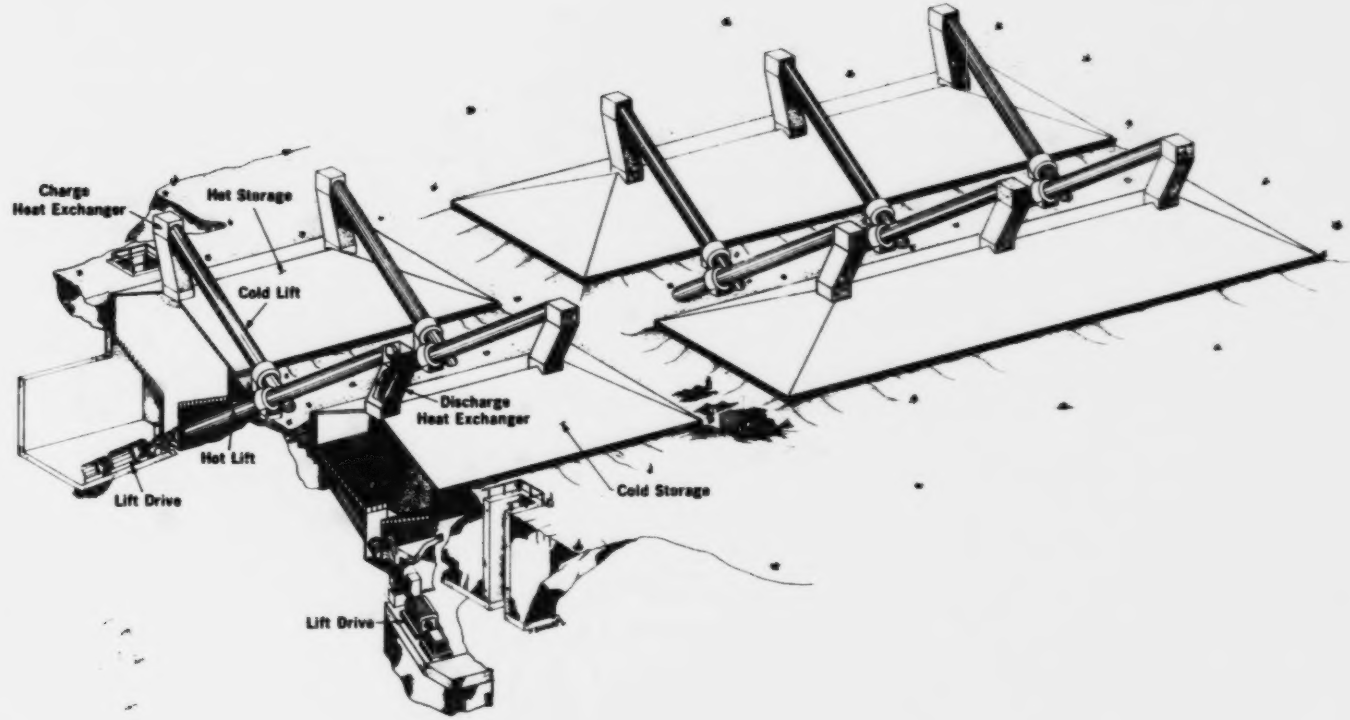

Charge Heat Exchanger
Hot Storage
Cold Lift
Discharge Heat Exchanger
Hot Lift
Lift Drive
Cold Storage
Lift Drive

Figure 1.

Moving Bed Thermal Energy Storage System Arrangement

A budgetary cost estimate was prepared, including all major components and systems. The total cost was estiamted at \$26.2 million in June, 1980, dollars. A breakdown of energy- and power-related costs are:

MBTESS Energy-, Power-, and Specific-Related Costs (June 1980 $\$ \times 10^3$)

Energy Related Cost, C_s

Item	Direct Field Cost	Indirect Cost
Excavation	\$ 97	7
Backfill and Compaction	662	125
Foundations and Footings	92	10
Storage Structure	3,427	629
Insulation	362	105
Medium	1,802	--
Subtotal	6,442 +	876
Subtotal =		\$7,318
Contractor's Profit		732
Engineering		552
TOTAL		\$8,602

Power Related Cost, C_p

Item	Direct Field Cost	Indirect Cost
Lifts	\$ 7,461	731
Piping	380	18
Heat Exchangers	4,978	171
Aux. Equipment	181	16
Controls and Inst.	279	--
Equipment Covers	337	74
	13,616 +	1,010
Subtotal =		\$14,626
Contractor's Profit		1,463
Engineering		1,463
TOTAL		\$17,552

TOTAL COST: \$26,154

The reference design was assessed with respect to potential limitations and potential improvements. Special equipment design or operating procedures required to control component wear to acceptable levels must be defined by testing. The heat exchanger configuration and performance must also be confirmed by testing. The thermal storage material was assumed to be silica sand (SiO_2) with a 30° angle of repose.

Assessment of safety, environmental, and land-use aspects revealed no unique constraints; and none are expected due to the chemically inert medium. Dust control measures will be required, but these methods are considered to be well known.

MBTESS FOR HIGH TEMPERATURE APPLICATIONS

As a part of the Phase I Study, an assessment of the reference design at higher storage temperatures was made and revealed substantial potential improvements in cost and performance. The total system cost for high temperature application was estimated to be \$10.5 million in June, 1980, dollars compared to \$26 million for the reference design. The reference design developed is considered applicable to storage temperatures up to 538C (1000F) with only minor modifications. At a 538 (1000F) charge temperature, 62% less storage material and tankage are required due to the increased stored energy density. Savings in power-related equipment also result from reduced material flow rates. These savings are reflected in the breakdown of energy- and power-related costs for 538C (1000F) storage given in the following table. Higher temperature reduces the number of lifts and their associated equipment. In addition, the turn-around efficiency will improve due to reduced pumping power and heat lossess. The prime modification would be in the roof and foundation of the tanks and using stainless steel 304 for the heat exchanger and lift construction.

High Temperature, 538C (1000°F) MBTESS Energy-, Power-, and Specific-Related Costs (June 1980 $ x 10^3)

Energy Related Cost, C_s

Item	Direct Field Cost		Indirect Cost
Excavation	$ 38		3
Backfill and Compaction	258		49
Foundations and Footings	36		4
Storage Structures	1,352		245
Insulation	141		41
Medium	703		--
Subtotal	2,528	+	342
	Subtotal	=	$2,870
	Contractor's Profit		287
	Engineering		217
	TOTAL		$3,374

Power Related Cost, C_P

Item	Direct Field Cost		Indirect Cost
Lifts	$2,542		$ 249
Piping	423		10
Heat Exchangers	2,174		57
Aux. Equipment	181		16
Controls and Inst.	115		--
Equipment Covers	112		25
Subtotal	5,547	+	357
	Subtotal	=	$5,904
	Contractor's Profit		590
	Engineering		590
	TOTAL		$7,084

TOTAL COST: $10,458

Temperature diagrams for candidate power cycles are shown in Figures 2 and 3. Figure 2 illustrates a relatively simple 410C/10.1 MPa (950F/1465 psia) cycle without reheat operating in both the charge and discharge modes. Figure 3 shows a more advanced steam cycle with 510C/16.55 MPa (950F/2400 psia) and 310C (950F) reheat. Round-trip efficiency for either cycle is estimated to be better than 90%.

Figure 2. Temperature Diagram for High-Temperature, Single-Stage Storage Using 1450 psi, 950F Steam Cycle in Charge and Discharge Modes

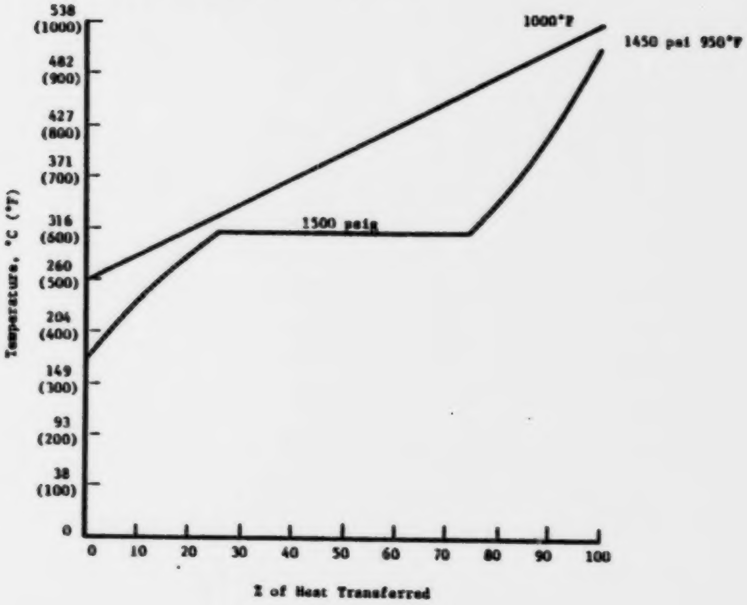
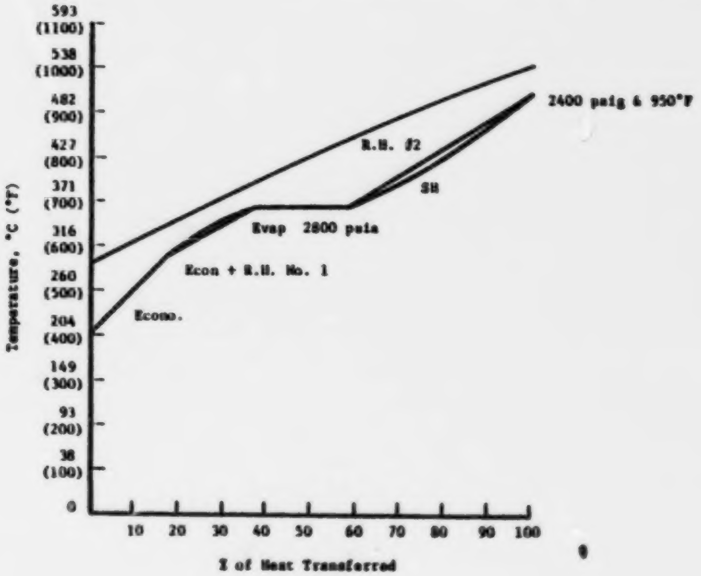


Figure 3. Special Temperature Diagram for Solar Plant Using High-Temperature Thermal Storage and Reheat Steam Cycle With Reduced Final Feed Temperature and Two-Stage Reheat in Charge and Discharge Modes



DEVELOPMENT ACTIVITIES FOR MBTESS

Technical issues in the moving sand bed concept discussed previously require resolution through a program of laboratory subscale experiments to establish bed material behavior in system components, the most important of which is considered to be the heat exchanger. A bed material program was defined to identify candidate materials and characterize their behavior under simulated laboratory conditions. A heat transfer and flow-study program was also defined to determine the flow distribution and heat transfer coefficients of the candidate bed materials in the heat exchangers. A development plan was also prepared for a subsystem research experiment leading to a commercial-scale design.

CONCLUSION

The principal conclusion of this study is that a thermal energy storage concept can be developed which is capable of operation over a wide temperature range and which is compatible with all major receiver working fluids. The system has a greater single-stage storage potential and the capability to be operated at a 538C (1000F) charge temperature and a low-discharge storage temperature. This provides a high storage energy density with the absence of considerations associated with media phase change (freezing). The concept offers greatly improved economics for high-temperature applications, especially for long discharging times. At medium temperatures, the system provides a backup to the oil/rock thermocline concept in the event that oil fill/replacement costs should exceed the projected range.

REFERENCES

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2. Contract, Sandia Laboratories No. 20-2990A, Advanced Thermal Energy Storage Concept, August 11, 1980.

3. Central Receiver Solar Thermal Power System, Phase I CRDL Item 2, Pilot Plant Preliminary Design Report, Volume 5, Thermal Storage Subsystem, SAN/1108-8/5, Sandia Laboratories.

PROJECT SUMMARY

Project Title: Advanced Solar Thermal Energy Storage Concept - Solar Mid-Temperature Application

Principal Investigator: Gerald F. di Lauro

Organization:
Combustion Engineering, Inc.
Nuclear Power Systems
Advanced Development Department
Windsor, CT 06095

Project Goals: Develop the conceptual design of a thermal energy storage subsystem utilizing the latent heat of fusion in the mid-temperature range (200-370°C, 400-600°F) for use with water/steam cooled receivers and for the production of saturated steam for industrial process heat applications.

Project Status: The project has been completed and the final report issued.

Based mainly on operating experience and development risk several promising concepts were selected from a wide variety of active and passive latent heat storage subsystems. Initial design development and cost estimate of major components using consistent groundrules narrowed the concepts to the passive tube intensive, direct contact heat exchange using an oil intermediary, and an active, mechanical scraper concept. The passive tube intensive was selected based on potential cost improvements, minimal developments needs, and high reliability of passive systems. A eutectic mixture of $NaOH/NaNO_3$ was selected for the phase change material mainly due to the melting temperature, and compatibility with carbon steel and aluminum.

The conceptual design of a tube intensive design using finned tubes was developed. Performance evaluation of the unit during an equilibrium daily duty cycle was determined. The static stability of the discharge process was evaluated, and the Ledinegg criteria was satisfied with no problem of flow maldistribution of discharge steam expected.

A budgetary cost estimate of the entire storage island which includes all components, site preparation and foundation was prepared. Both shop door costs and sell price were obtained. Design and cost improvements were identified. A cost comparison was made with a first generation, oil/rock storage subsystem sized on the same basis as the latent heat subsystem. A cost advantage for the latent heat subsystem of 22-34% over the oil/rock subsystem was identified based on shop door cost of major components.

Contract Number: SAND 20-2990-B

Contract Period: August 25, 1980 through March 31, 1981

Funding Level: $146,919

Funding Source: U.S. Department of Energy through Sandia National Laboratory, Livermore, CA

CONCEPTUAL DESIGN OF A LATENT HEAT THERMAL ENERGY STORAGE SUBSYSTEM FOR A SATURATED STEAM SOLAR RECEIVER AND LOAD

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The conceptual design of a tube intensive latent heat thermal energy storage (TES) subsystem utilizing a eutectic mixture of sodium hydroxide and sodium nitrate as the phase change material (PCM) has been developed. The charging and discharging of the unit is accomplished by the same serpentine tube bundle heat exchanger in which heat transfer is augmented by aluminum channels acting as fins. Every tenth channel is made of steel to provide tube support. A tube bundle is composed of 15 rows of 15.9 mm (0.625 in) O.D. tubes 15.2 cm (6.0 in) apart. Each row is a single tube approximately 78 m (255 ft) long formed into a vertically oriented serpentine. The horizontal runs of the tube are 15.2 cm (6.0 in) apart. The aluminum channels are inserted between the horizontal runs and connect all the tube rows. This assembly is strapped together and the tubes connect to the steam and condensate headers. Five of these bundles are contained in a single rectangular tank which is nominally 4 m x 4 m x 11.6 m (13'x13'x38'). Eight tanks are required to achieve the 148 MWh capacity and 30 MW peak charge and discharge rate established for this study.

The solar receiver produces saturated steam at 288°C (550°F) and the excess over demand is charged into the PCM at 260°C (500°F) by condensing steam. During discharge of the TES saturated water is covered to saturated vapor at 232°C (450°F). A simple solar heat rate and constant demand were assumed.

The augmented heat transfer design resulted from an analytical effort which examined the freezing of salt over the discharge process in a unit cell surrounding a heat transfer tube. The two-dimensional, finite-difference calculations were performed by computer program FREEZE written for this effort. The study included the determination of the effects of conductivity enhancement and extended heat transfer surfaces of various configurations. Tube diameter and spacing were parametrically varied to assess geometric impact. Both steel and aluminum fins were considered. The final design configuration was simulated in the FREEZE model. The spacing of the heat transfer tubes was determined by finding when the target capacity, the peak discharge heat transfer rate, and virtually complete freezing of the PCM occurred simultaneously.

Performance characteristics for the TES unit were obtained with a modified version of the computer program TESST (1) which calculates the PCM temperatures, and the charging and discharging steam temperature distribution and pressure drop over the daily duty cycle. The effect of the fins was simulated by an enhanced value for the PCM thermal conductivity. The value was selected by matching the results from the FREEZE code. At beginning of discharge the PCM is virtually all liquid with 28°C (50°F) of superheat at the top of the unit. As discharge proceeds the salt superheat at the top begins to reduce, and the salt starts to freeze at the bottom. Towards the end of discharge the bottom of the unit is subcooled solid and the top is at the melting point of the PCM. There is thus a thermocline which provides some sensible heat storage in addition to latent heat storage.

During discharge saturated water enters the bottom of the unit, boils uphill and emerges at the top. During the early stages of discharge the unit produces steam with 45-50°C (80-90° F) of superheat and, towards the end of discharge, steam with quality as low as 88-90%. For service applications in which a high degree of superheat is undesirable, a desuperheater can be used to reduce the level of superheat using subcooled water from the process. Alternatively, some of the saturated water entering the TESS could be by-passed and mixed with the effluent, and thereby bring the temperature within the desired range.

The stability of the boiling process was examined. At various stages during the discharge process the flow through the tubes was varied from 10% to 200% of the maximum flow, and the pressure drop through the two-phase and superheat regions was calculated. The total pressure drop including friction, acceleration, and elevation components shows a positive, monotonic variation with flow rate. The Ledinegg static stability criterion was thereby easily satisfied, so flow maldistribution of the discharging steam is not expected.

A budgetary cost estimate for the final design is $\$3.878 \times 10^6$ for the sell price of the total TES island. This includes the cost of materials and fabrication of the hardware; shipping to the site (using Chattanooga, TN to Barstow, CA as representative); site preparation and foundation; tank unloading from rail cars, moving, and installation; and installing piping, insulation, and lagging. The sell price reflects standard contingency, G&A and margin mark up on the shop door costs. A total shop door cost of $\$2.93 \times 10^6$ is indicated. The estimate does not include engineering costs, sales tax, or cost of money. It does include the material cost of the salt eutectic but not the filling of the tanks. Cost for the tank fill was not available at the completion of this effort, but it is expected to be relatively small.

Based on preliminary calculations, a bare-tube version of the final design was estimated. More than 5 times the finned-tubing length was required for the 15.9 cm (0.625") O.D. tube. The shop door cost and sell price of the tubes are $\$1.36 \times 10^6$ and $\$1.89 \times 10^6$, respectively. These are $\$2.67 \times 10^5$ and $\$3.71 \times 10^5$ more than the corresponding costs of the tubing and fins in the final design. Thus, the use of fins to augment heat transfer is a definite cost improvement.

Close examination of the final calculation results from FREEZE and TESST indicated areas of conservatism in the component sizes of the final design. Taking advantage of thermocline formed in the PCM, which yields substantial solid subcooling and liquid superheat, approximately 4.5×10^5 kg (100×10^6 lb) of PCM can be saved. This reduces the number of containment tanks and the associated shipping costs. The heat transfer length is largely the same as estimated by the results of FREEZE; however, the spacing must be reduced because of the small volume of PCM. Savings in the amount of fins and tube bundle supports are realized. Additional savings can be obtained by increasing the fin spacing to 2.5 cm (1.0"). The reduced heat flux necessitates a 12% increase in tube length, but this increase is far outweighed by the reduced cost of the fins. These design improvements can reduce the shop door costs and sell price of the reference final design by as much as $\$5.31 \times 10^5$ and $\$7.38 \times 10^5$, respectively.

The main objective of this study is to develop a latent heat TESS which shows a cost advantage over the oil/rock sensible heat storage. For comparison during the selection process, an oil/rock benchmark was developed in which the major components were sized and costed. These costs amounted to $\$2.10 \times 10^6$ to $\$2.46 \times 10^6$ for volume utilization factors in the range of 80% to 60%, respectively. A 3½% loss of oil per year was estimated for the service condition under consideration. In addition, foundation costs were scaled based on the latent heat cost estimate for a foundation design like that of the Barstow plant. The sum of the component costs and capitalized operation and maintenance costs is between $\$2.38 \times 10^6$ to $\$2.81 \times 10^6$ for the range of utilization factor values. In order to compare the latent heat TESS to the oil/rock system, the shop door cost of the major components (containment tanks, PCM, tubes and fins, and foundation) was determined. For the reference design, this is $\$2.34 \times 10^6$; and $\$1.85 \times 10^6$, for the improved design. The shop door cost of the improved design is 22-34% less than the corresponding cost of the oil/rock sensible heat TES.

The passive tube-intensive concept was selected from a large variety of candidate concepts. Selection criteria based on costs for the major components, and the state-of-the-art and reliability of the unit were established. The most promising concepts in the literature were roughly sized, and costs estimated. The designs considered were: (1) the tube-intensive concept with and without conductivity enhancement; (2) macroencapsulation of the PCM with direct charging and discharging by steam, and indirect charging and discharging using oil as an intermediate (Chubb concept); (3) direct contact heat exchange using oil (e.g., biphenyl) or liquid metal (Pb·Bi) as the intermediary fluid between discharging steam and the PCM; and (4) mechanical devices to scrape the solid PCM from the heat transfer surface during discharge. An oil/rock sensible heat TESS was established for benchmark comparisons.

The encapsulation concepts were immediately eliminated due to high component costs. The Chubb boiler tank had an estimated cost of $\$3.5 \times 10^6$ to $\$6.1 \times 10^6$. This was high, compared to the tube intensive concept cost estimate $\$2.0 \times 10^6$ to $\$2.5 \times 10^6$, and the oil/rock system estimate, $\$2.1 \times 10^6$ to $\$2.5 \times 10^6$. The direct charging/discharging macroencapsulation concept required costly pressure vessels and had an estimated cost between $\$11.6 \times 10^6$ and $\$12.7 \times 10^6$. The mechanical scraper concepts were estimated to cost in the range of $\$1.8 \times 10^6$ to $\$2.4 \times 10^6$. The direct contact heat exchange concept using lead·bismuth initially showed higher cost than the oil systems. Further effort showed comparable cost in the area of $\$2.5 - \$3.0 \times 10^6$, with the oil system showing about a 15% lower cost.

Based on these costs the candidates were narrowed down to the tube intensive design, the direct contact concept and the vertical mechanical scraper. These concepts all showed comparable costs within the limits of the sizing and cost assumptions. The passive tube intensive design was selected since potential for cost improvements was still possible using augmented heat transfer methods, the design required little in the way of development program support, and it had the inherent reliability of a purely passive system.

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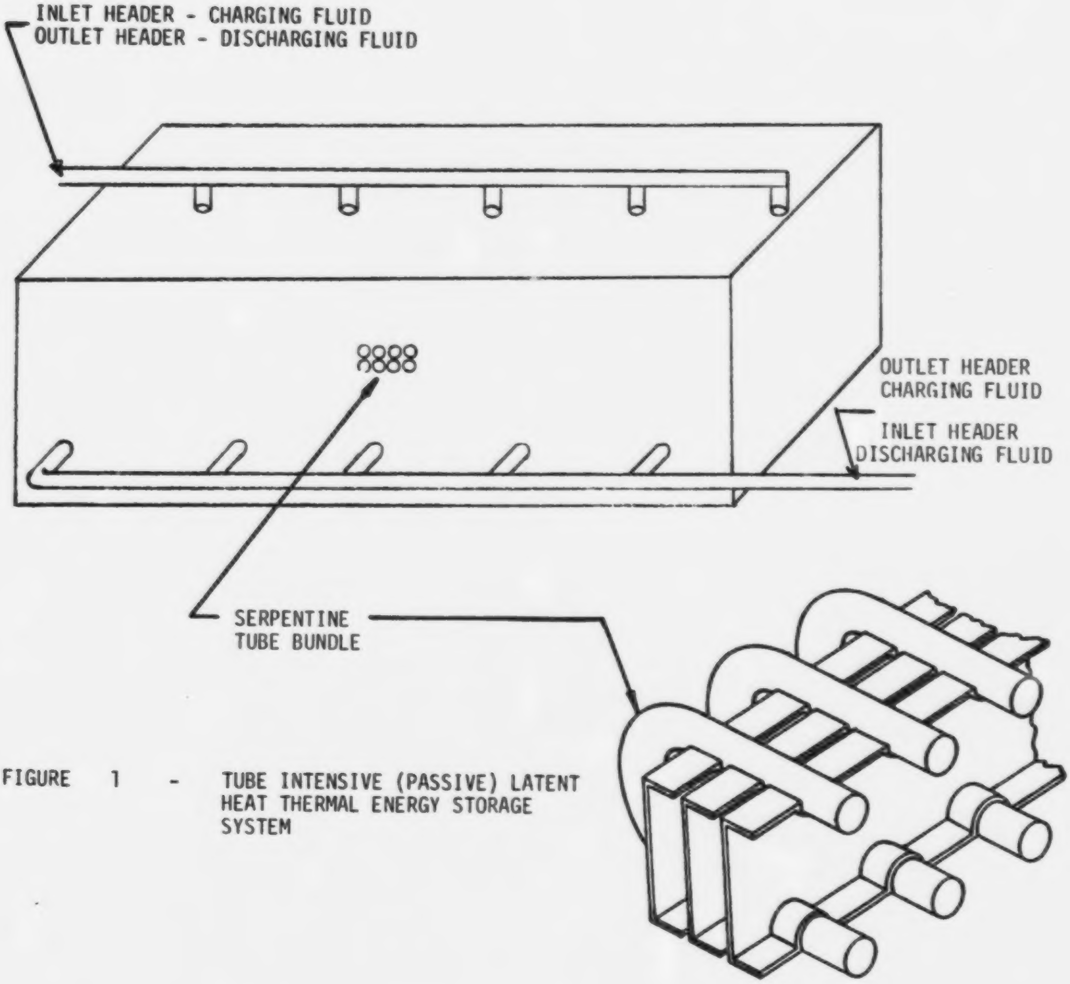
INLET HEADER - CHARGING FLUID
OUTLET HEADER - DISCHARGING FLUID
OUTLET HEADER
CHARGING FLUID
INLET HEADER
DISCHARGING FLUID
SERPENTINE
TUBE BUNDLE

FIGURE 1 - TUBE INTENSIVE (PASSIVE) LATENT HEAT THERMAL ENERGY STORAGE SYSTEM

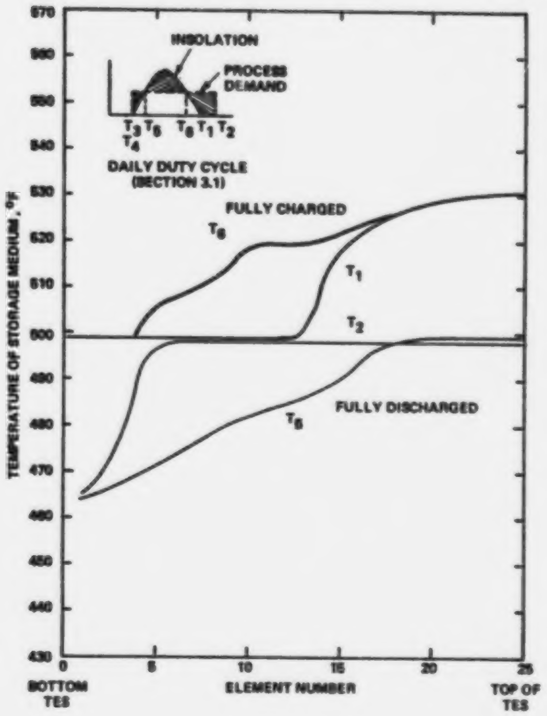

FIGURE 2

VERTICAL TEMPERATURE PROFILE OF STORAGE MEDIUM

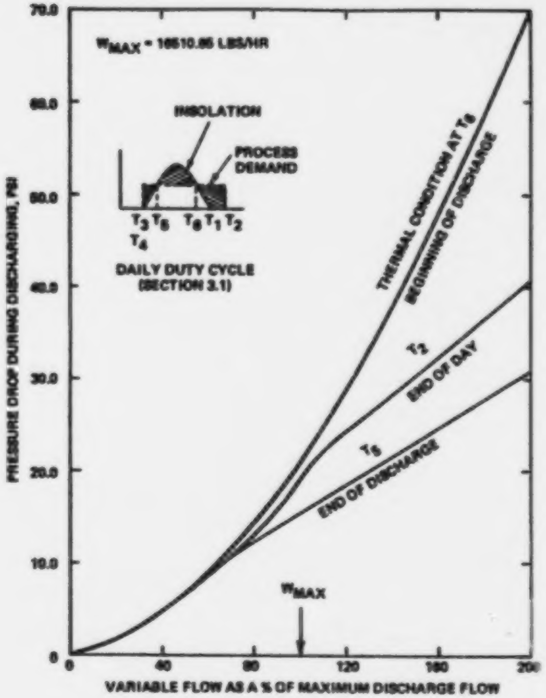

FIGURE 3

STATIC FLOW STABILITY CURVE

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TABLE 1

THERMAL ENERGY STORAGE SYSTEM BUDGETARY COST ESTIMATE

(Island Cost w/o Engr.)

Hardware	Shop Door Cost	Sell Price 2/81
8 Tanks @ $45,500 ea. (Incl'd prime coat)	$364,000	$ 506,500
40 Tube bundle support structure @ $1,925 ea.	77,000	107,200
50,000 lb. tubing & piping	262,000	364,600
230 miles, tubing (161,920 pieces) aluminum & steel fins, fabrication, and assembly	832,000	1,158,300
8 Sets of tank insulation & aluminum jacket	73,000	101,600
Freight (rail) Chatt., Tn to Barstow, CA	88,000	136,400
General liability insurance @ $0.31/$100	5,800	7,400
HARDWARE TOTAL		$2,382,000
Installation		
Field Construction Cost		$ 369,500
Materials:		
Eutectic (NaOH-NaNO$_3$), 4.8x10^6 lb	871,000	1,102,300
Concrete, Rebar, Gravel	15,400	19,500
General Liability insurance @ $0.31/$100	3,700	4,700
INSTALLATION TOTAL		$1,496,000
Total present day budgetary sell price, delivered, and erected, subject to escalation from 2/81, w/o engineering, sales tax, and cost of money.		$3,878,000

TABLE 2

LATENT HEAT VS. OIL/ROCK SENSIBLE HEAT STORAGE

LATENT HEAT

	Reference Design	Improved Design
Tanks	$ 364,000	$ 273,000
Tubes	262,000	293,000
Fins	832,000	579,400
Tube Bundle Supports	77,000	61,500
Salt	792,000	628,300
TOTAL COMPONENT COST	$2,327,000	$1,835,000
Foundation	15,400	11,600
TOTAL	$2,342,000	$1,847,200

OIL/ROCK SENSIBLE HEAT

	80% Utilization	60% Utilization
Tanks	$ 657,000	$ 756,000
Oil	603,000	798,000
Rocks	201,000	266,000
Heat Exchanger	562,000	562,000
Pumps	54,000	54,000
Piping	26,000	26,000
TOTAL COMPONENT COST	$2,103,000	$2,462,000
Foundation	114,600	141,700
Operating & Maintenance	158,300	205,800
TOTAL	$2,375,900	$2,809,500

SAND81-1868C

SINGLE MEDIA THERMOCLINE TES STUDIES AT SANDIA NATIONAL LABORATORIES

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ABSTRACT

The status of thermocline thermal energy storage (TES) development at Sandia National Laboratories is summarized. The work centers around testing in the 1200 gal engineering prototype thermocline test facility. The results of heat loss, charge, discharge and static tests in the prototype tank are described. Also described are analytical work and a supportive laboratory-scale program which is investigating diffusers to inhibit mixing in the tank.

INTRODUCTION

Thermal Energy storage (TES) can greatly affect the economics of solar thermal systems. The thermocline TES system consists of a single tank storing the hot fluid above the cold fluid, using the natural buoyant forces to keep the two layers separated. Assuming that the losses which contribute to the degradation of the thermocline system can be eliminated or minimized, thermocline TES is attractive because of its simplicity, low capital costs and low maintenance costs.

Although numerous experimental studies concerning the stratification of liquids have been reported in the literature,[1-8] a definitive answer concerning the feasibility of the thermocline TES concept for reasonably sized solar thermal systems has not emerged. To further study the concept, a large thermocline storage test facility has been constructed at Sandia National Laboratories, Albuquerque. Specific objectives were: (1) to build the most efficient thermocline storage system based on present knowledge, (2) instrument the system sufficiently to obtain data on the important physics of the system, (3) to minimize scaling effects, (4) to use conventional hardware as much as possible for economic considerations, and (5) keep enough flexibility in the design to incorporate improvements in the system as the investigation brings about additional understanding.

In addition to the testing of the large-scale prototype thermocline tank, two other supportive efforts are being conducted. A laboratory-scale program was initiated to investigate diffuser designs which will minimize mixing at the inlet and outlet of the tank. Also, analytical work is being done to develop a predictive capability of thermocline performance.

THE LARGE-SCALE PROTOTYPE THERMOCLINE TANK

Five loss mechanisms which degrade the efficiency of a thermocline storage system are: (1) heat loss to ambient, (2) convection induced by heat transfer at the tank walls, (3) mixing at the inlet and outlet, (4) thermosiphoning at the inlet and outlet manifolds, and (5) thermal conduction from the hot layer to the cold layer. In the large-scale prototype thermocline tank, the first two loss mechanisms were dealt with by building the tank with thin walls and placing sixteen inches of fiberglass insulation around the tank. Diffusers were placed at the inlet and outlet to reduce mixing. Valves were placed as close as possible to the inlet and outlet to minimize thermosiphoning. No action was taken to reduce the diffusion between layers because this effect is small.

The thermocline tank resulting from the design effort has a 1200 gal capacity and is instrumented with 384 thermocouples and 5 flowmeters. Therminol-66 is the working fluid. The system is designed to operate at 600°F on the hot side and 400°F on the discharge side. Fig. 1 shows an internal view of the tank and its instrumentation. A more detailed description of the hardware may be found in reference 14.

A series of tests were conducted to determine the heat loss from the tank to the environment and to verify that the losses are not significantly different from predictions. Previous storage tanks tested at SNLA have lost 5 to 10 times the energy originally anticipated and, consequently, were unsuitable as TES systems. The tests were to provide a heat flux boundary condition necessary for a one-dimensional analytical model.

The results from these tests showed that the actual heat loss from the tank is 60 to 100% higher than anticipated. For example, with the fluid at a uniform temperature of 500°F, the total predicted heat loss was approximately 2000 Btu/hr compared to a measured heat loss of 3980 Btu/hr. Part of the discrepancy is known to be due to a thermosiphon loop that existed in the top manifold during these tests. Other data suggest that thermosiphoning can contribute at least 800 Btu/hr to the heat loss. A future test is designed to determine if thermosiphoning can account for the entire discrepancy between theory and experiment. If not, then an additional heat loss mechanism will need to be identified. In any case, thermosiphoning can be easily eliminated by draining the upper manifold whenever the system is placed in a static condition. Conservative calculations show that, if the thermosiphon loop is eliminated, the energy loss in the thermocline tank should be less than 4.8% a day at the upper operating temperature of 600°F.

A typical cool-down curve depicting energy in the tank versus time is shown in Fig. 2. Note that the exponential least-squares curve fit described by the equation

$$Q_{tank} = (Q_{tank})_{init} \cdot \exp[Bt]$$

is in good agreement with the experimental data. Here, Q_{tank} is the energy in the tank, t is time and B may be termed the heat loss time constant for this particular TES system. The value of B, $0.00215 \pm .00015\ hr^{-1}$, was consistent for the three heat loss tests that were performed. This consistency suggests a simple method for characterizing the heat loss from thermocline TES systems in general.

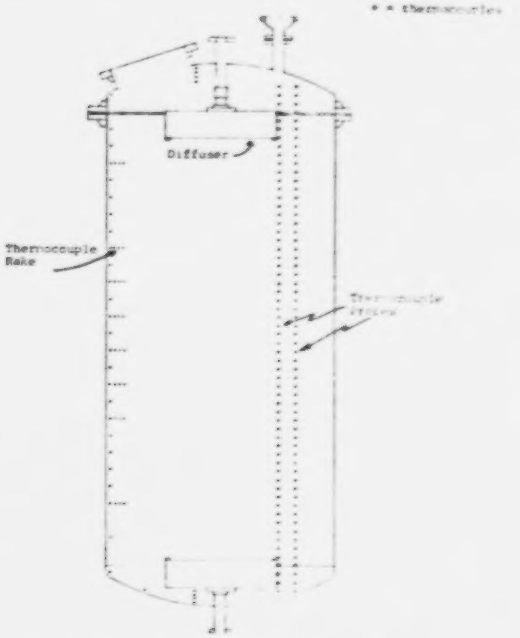

Fig. 1 Internal View of the 1200 gal. Prototype Thermocline Tank and Instrumentation

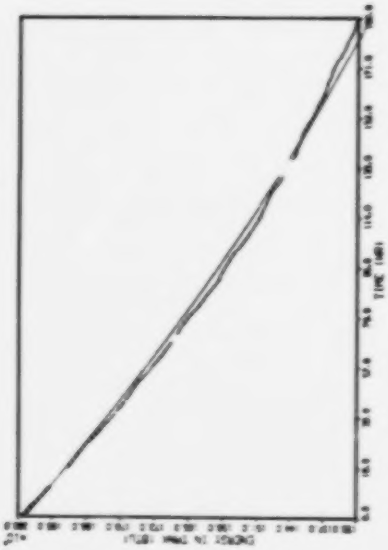

Fig. 2 Time vs. Total Energy in the Thermocline Tank During A Cool Down Test

A series of charge (or discharge) and "hold" tests have also been performed in the large-scale thermocline tank. The purpose was to examine the role of the diffuser in determining the initial extent of the thermocline region, and to examine the thermocline's degradation with time when placed in the static mode. In a charge test, 600°F fluid was pumped into the tank which was filled with fluid at a uniform temperature of 400°F with a flow direction from top to bottom. In a discharge test, the tank was filled with 600°F fluid and 400°F fluid was pumped into it from below. When the thermocline reached a desired location in the tank, flow was shut off and the tank was placed in a hold condition.

At the time that the large-scale thermocline tank was undergoing shakedown testing, lab-scale testing of the then current diffuser design showed it to be ineffective in preventing mixing. It was decided to perform the series of charge/discharge tests using the ineffective, existing diffuser while a more effective one was developed from small-scale experimental testing. The improved diffuser design would then be placed in the large-scale tank and tested in the same charge/discharge test series as the original diffuser. The importance of the diffuser would be indicated by comparing the relative effectiveness of the two diffusers in inhibiting mixing.

To date, only the test series using the original diffuser has been performed. The results indicate that, for a discharge, fairly sharp thermoclines can be obtained at flow rates up to 10 gpm. Since this corresponds to a 100% fluid turnover time of 2 hours for the 1200 gal tank, the flow rate must be considered high for this TES system. Fig. 3 illustrates the thermocline obtained from a discharge test with a flow rate of 9 gpm. The thermocline width is 22 inches. The two horizontal lines crossing the width of the graph indicate the location of the top and bottom diffusers. The three thermocouples indicating cooler temperatures about 15 inches above the top diffuser are located in the nitrogen cover gas placed in the tank to keep the pressure uniform. The results from charging tests were not as encouraging as the discharge tests. Even with flow ratesd as low as 3 - 5 gpm, satisfactory thermoclines were not obtained. Considerably more mixing occurs when flow is from top to bottom than when it is from bottom to top. Although it is not yet clear why this occurs, this significant mixing proves the diffuser to be extremely important in contributing to the overall system efficiency, especially at high flow rates.

All of the static tests showed that the hot upper layer in the tank loses a substantial amount of energy while the cold layer becomes highly stratified. Fig. 4 illustrates these changes by showing the thermocline of Fig. 3 25.5 hours into the static test. Part of the reason why the bottom cold layer exhibits diffusion while the upper layer does not is that heat is lost through the bottom of the tank while the top is insulated by the nitrogen cover gas. In addition, the flow fields in the top and bottom layers may be different. The fluid in the thermal boundary layer in the top of the tank is convected downward due to heat loss to ambient and heat loss to the lower cold layer. However, the cold fluid boundary layer is driven by conflicting phenomena. Heat loss to ambient imparts a downward convective motion to this fluid while heat gain from the hot layer counteracts that behavior. The different convective motions caused by each layer's unique physics offers an additional explanation for each layer's different response to a cool down test. Finally, thermosiphoning was occurring in both the upper and lower manifolds in this test series. While it is not fully understood, clearly the significant heat loss caused by thermosiphoning must play a role in determining the results of the cool down tests. Its role will be determined more definitively when the thermosiphon loop is eliminated in future cool down tests.

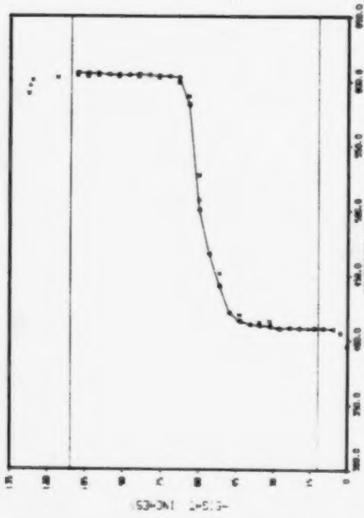

Fig 3 Axial Temperature Distribution in the 1200 gal. Thermocline Tank at the Conclusion of A Discharge Test at Approximately 10 gpm

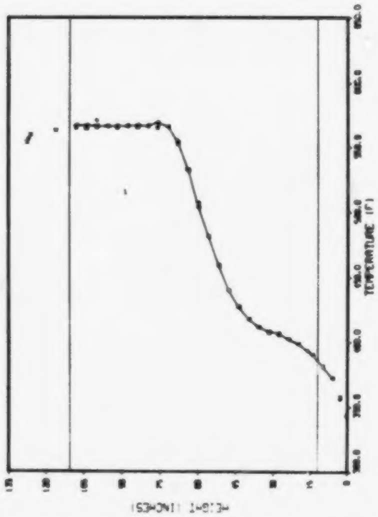

Fig. 4 Axial Temperature Distribution in the 1200 gal. Thermocline Tank During the Cool Down Test 25.5 Hours After the Shutdown Temperature Profile Shown in Fig. 3.

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DIFFUSERS

Ideally, the function of a diffuser is to transform the high velocity inlet fluid to a uniform low velocity across the entire diameter of the storage tank. As noted, data from the large-scale thermocline tank (and also from laboratory-scale tests) have demonstrated that the diffuser is an important component. It establishes the initial thermocline width and thereby fixes the maximum amount of high quality energy which may be later extracted from storage. Unfortunately, very little information was available on short axial-length, high area-ratio diffusers. Thus, a laboratory-scale effort was initiated to test and determine the governing parameters for such diffusers.

The diffuser needs to operate satisfactorily over a broad range of temperatures and flow rates. It was also required to be compatible with Therminol-66, have low weight, a short axial dimension, and have as small a pressure drop as possible commensurate with satisfactory performance.

The lab-scale research effort has led to the diffuser design shown in Fig. 5. Its major components are a perforated plate and wire mesh. The perforated plate changes the single high velocity jet at the tank inlet into many, high velocity jets distributed evenly over the diffuser's outlet. To prevent mixing, these small jets must be slowed and spread until they coalesce into a uniform slug-like flow. The multiple layers of wire mesh perform this function. Since the effective flow area in the wire mesh is very large compared to that of the perforated plate, the entire pressure drop caused by the diffuser can be considered to be that of the plate.

For an optimum effect, a diffuser should cover the entire cross-section of the tank. However, laboratory-scale tests have indicated that half-diameter diffusers can achieve thermoclines as sharp as those produced by full-diameter diffusers. This observation can be explained in part by the fact that the full-diameter diffuser has four times as much material as the half-diameter diffusers which the incoming hot fluid must bring up to temperature. Thus, there appears to be a trade-off between large area coverage and minimum heat capacity of the diffuser. This observation was convenient in that the large-scale diffuser contains instrumentation probes that effectively limit its diameter to 26 inches in a 54-inch diameter tank. Thus, two 26-inch diffusers of the type shown in Fig. 5 are presently being installed in the large-scale tank. Although scaling from laboratory to large scale introduces uncertainties concerning the performance of the new diffusers, their performance will certainly exceed that of the original 26-inch diffusers.

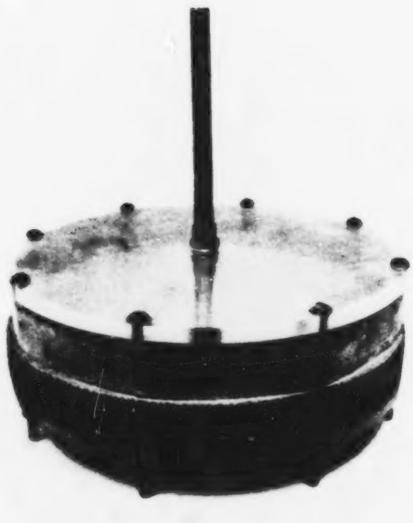

Fig. 5 The Small-Scale Diffuser Incorporating a Perforated Plate and Layers of Wire Mesh

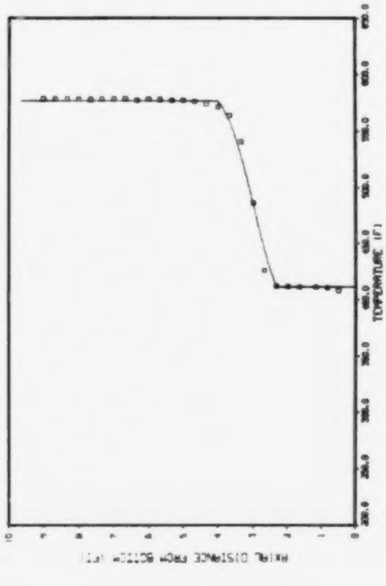

Fig. 6 Experimental and Curve-Fit Temperature Profiles in the 1200 gal. Tank at the Start of A Cool Down Test (▫ = Experimental data)

Since parasitic pumping requirements reflect unfavorably on the overall efficiency of thermocline TES, an important aspect of diffuser design involves minimizing the pressure drop across the perforated plate. At the same time, care must be taken to insure that the pressure drop is sufficient to force the flow out to the plates full diameter; otherwise, backflow results near the outer edge.

The pressure drop across the plate for large tanks should be in the range of 1 - 2 psi[9]. Since the thermocline tank is expected to operate across a broad range of flow rates and pressure drop varies with the square of flow rate, meeting this requirement for all operating conditions is not possible. In addition, the traditional approach in computing pressure drop across a flow constriction of this type has been to lump all of the flow losses in a discharge coefficient. However, there appears to be no available data which can account for all of the physics associated with the porous plate diffuser, i.e. nonuniform approach velocity profile, incompressible flow, multiple round holes, low Reynolds number, very low porosity. Thus, although diffuser design requirements dictate that accurate pressure drop information is necessary, to date only estimations on discharge coefficients exist. Such data will become available from differential pressure drop instrumentation installed in the new top diffuser in the large-scale thermocline tank. By conducting a series of flow tests at different flow rates, and measuring the pressure drop across the plate, the discharge coefficient and its dependence on flow rate will be determined. This data will aid in determining the proper porosity of the perforated plate in future diffuser designs.

ANALYTICAL WORK

The approach developed by Rahm and Walin[10,11,12] provides a simple one-dimensional analysis of the stratification induced by natural convective flow in a thermocline TES system. The model requires a knowledge of a modified heat transfer coefficient along the vertical walls of the tank and assumes that the top and bottom are perfectly insulated. The Rahm-Walin model was used to examine some of the large-scale static test results. Fig. 6 shows the actual and predicted temperature profile used as an initial condition to the model at the start of a static test. Figure 7 compares the actual and predicted temperature profiles 18.5 hours later. Theoretical agreement with the data in the upper hot layer is excellent. The cold bottom layer experiences more diffusion than predicted by the model. Reasons for the high diffusion rate have already been discussed. At present, the modified heat transfer coefficient used in the Rahm-Walin model is chosen by trial and error to properly account for the overall heat loss. In the future, an effort will be made to calculate the heat transfer coefficient directly from the heat loss data.

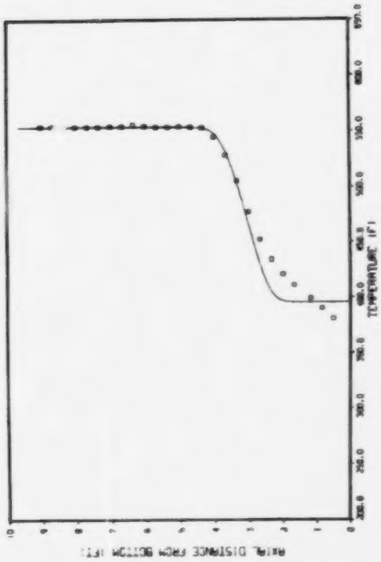

Fig. 7 Comparison of the Rahm-Walin to the Experimental Temperature Distribution in the 1200 gal. Tank 18.46 Hours Into a Thermocline Cool Down Test (ø = Experimental data)

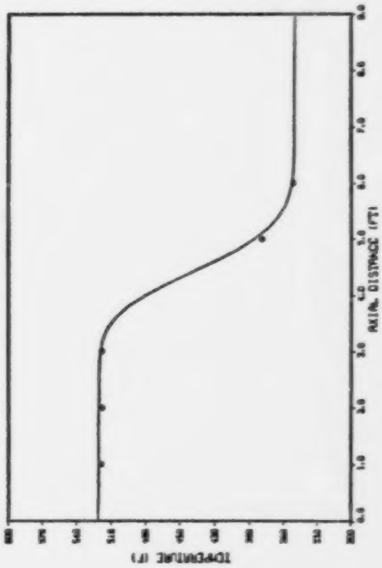

Fig. 8 Comparison of the Mixing Model With Experimental Data for a Charging Process at 5 GPM and 1.5 Hours Into the Simulation

The Rahm-Walin model is limited to the case where the thermocline TES system is in a static mode, i.e. no flow. It is also desirable to be able to predict the stratification which is established during charging and discharging of the system. These processes depend crucially on the inlet and outlet conditions and hence, on the diffuser design. As noted previously, the sharpness of the thermcline during charging is a strong function of the degree of mixing at the inlet.

An approach by Han and Wu[13] is particularly appropriate for those situations where the entering fluid falls (or rises) through the relatively stationary fluid which originally fills the tank. Conversely, when the charging fluid penetrates the stationary fluid only to a limited extent dictated by the momentum of the entering fluid and its relative buoyancy, the entrainment model of Han and Wu is not appropriate. An alternate analysis proposed by Han and Wu for the latter situation does not conserve energy and can thus lead to erroneous results.

At SNLA, a simple one-dimensional model of the mixing process which occurs at the inlet was developed for the analysis of charging (or discharging) processes which do not result in the entering fluid falling (or rising) through the fluid in the system. The model requires a knowledge of the penetration depth of the entering fluid as well as a parameter which is a measure of the degree of mixing associated with the entering stream. Based on rational estimates of these quantities, a numerical simulation of a typical low-flow charging process was performed for the large-scale tank. Initial results are compared with experimental data in Fig. 8. A somewhat closer fit to the experimental data could be obtained by varying the parameters in the model. However, this approach involves a degree of arbitrariness which we wish to avoid. Additional experimental data is required in order to fully characterize the system and provide best estimates for the parameters in the model.

We anticipate that the SNLA mixing model together with the Rahm-Walin model will provide a reasonably complete analytical coverage of the processes which occur in large-scale thermocline TES systems.

ACKNOWLEDGEMENTS

I would like to acknowledge C. E. Hickox as the author of the one-dimensional mixing model and also D. W. Larson and P. C. Montoya for their contributions in diffuser design. All three are in Department 5510 at Sandia National Laboratories.

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PROJECT SUMMARY

Project Title:	Dish Mounted Latent Heat Buffer Storage
Principal Investigator:	Ram Manvi
Organization	Jet Propulsion Laboratory California Institute of Technology Pasadena, California 91109
Project Goals:	To develop appropriate dish-mounted Latent Heat Storage Subsystems for Rankine, Brayton and Stirling engines operating at 427°C, 816°C or 1370°C and 816°C, respectively. The task provides for storage requirements definition, conceptual design, media stability and compatibility tests and thermal performance analyses.
Project Status:	The buffer storage requirements for the dish mounted Rankine, Brayton and Stirling engines have been identified. High temperature (816°C) material corrosion experiments continuing with NaCl, Na-NaCl, $NaF-MgF_2$ contained in SS321, SS410 and 9 Cr-1MO alloy steel. The experiments include capsules and convection loops. Heat transfer enhancement experiments initiated with Na-NaCl. Transient heat transfer computer code assembled and runs made for the performance analysis of parabolic dish receiver integrated latent heat buffer storage. Advanced thermal energy storage concepts indentified for receiver operating at 1370°C.
Contract Number:	SLL Purchase Order 92-8908, Change 1.
Contract Period:	October 1, 1980 through September 30, 1981.
Funding Level:	$210,000
Funding Source:	U.S. Department of Energy through Sandia Laboratories, Livermore.

DISH-MOUNTED LATENT HEAT BUFFER STORAGE*

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ABSTRACT

A parabolic dish solar thermal power plant comprises a field of parabolic dish power modules. Each module is composed of a two-axis tracking parabolic dish concentrator which reflects insolation into the aperture of a cavity receiver at the focal point of the dish. The heat generated by the solar flux entering the receiver is removed by a heat trasfer fluid and is used to drive a small heat engine/generator mounted adjacent to the receiver. Since thermal buffer storage can improve upon system performance, a task is being conducted in support of the Thermal Energy Storage for Solar Thermal Applications Program (TESSTA). The objective of this task is to develop appropriate dish-mounted thermal buffer storage subsystems for Rankine, Brayton and Stirling engines operating at 427°C, 816°C, 1370°C and 816°C, respectively. This paper describes the effort completed or continuing during FY 1981 concerning storage requirements definition, conceptual design, media stability and compatibility tests and thermal performance analyses.

INTRODUCTION

As a first step toward commercialization of the modular-Point Focusing Distributed Receiver (PFDR) solar thermal electric system, the U.S. Department of Energy is planning a series of experiments to help establish their technical, operational and economic aspects. In these experiments small heat engines with attached electrical generators will be mounted adjacent to the receivers located at the focal point of each parabolic dish concentrator. The power conversion system requirements are the following:

1. Ranking cycle - 15 kW_e organic engine operating at ~427°C.
2. Brayton cycle - 18 kW_e open cycle Brayton engine operating at ~816°C or at ~1370°C in advanced systems.
3. Stirling cycle - 15 kW_e kinematic Stirling engine operating at ~816°C.

Since insolation varies with diurnal and seasonal cycles as well as with local cloud cover, the thermal energy entering the receiver is subject to corresponding time-dependent fluctuations. The heat removed from the receiver also fluctuates. These fluctuations, especially rapid fluctuations due to cloud cover, can be attenuated by incorporating latent heat buffer storage. The addition of thermal storage to receivers is referred to as "thermal buffering" since it provides a buffer between the variations in solar flux and the heat delivered to the heat engine. This buffering reduces engine part-load operation, improves efficiency and alleviates control requirements. Buffer storage also reduces engine start/stop cycles (resulting from cloud cover) which is an important factor in extending engine life.

The degree of attenuation or buffering provided by the receiver depends upon its thermal inertia, heat flow paths and control logic. Each power conversion unit requires a different amount of thermal buffering to handle variations in short-term insolation. Hence, a task was initiated during FY 1980 in support of the TESSTA Program to define the requirements for latent heat thermal energy buffer storage subsystems and for subsystem research experiments for point-focusing distributed receivers equipped with Rankine, Brayton and Stirling power conversion cycles. The storage requirement definition includes thermodynamic performance analyses to determine the need for thermal energy buffer storage

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* The program described in this paper is managed by the Jet Propulsion Laboratory, California Institute of Technology, for the U.S. Department of Energy through an agreement with NASA. The NASA Lewis Research Center supports the program in the area of power conversion.

TABLE 2. BUFFER STORAGE DESIGN REQUIREMENTS SUMMARY (Cont'd)

DESIGN CHARACTERISTICS	JPL REQUIREMENTS	HEDL SENSIBLE BUFFER HEAT RECIEVER	HEDL LATENT BUFFER HEAT RECEIVER
Gas Type (Working Fluid)	Air	Air	Air
Maximum Δ Temperature of Outlet Gas	1170 - 1370°C	1170 - 1370°C	1170 - 1370°C
Storage Time	30 min.	>30 min.	>30 min.
Receiver Mass	150 - 200 kg	~200 kg	~160 kg
Mass Flow of Gas for 60 kw Output	130 g/sec	130 g/sec	130 g/sec

The sensible heat storage is shown in Figure 1 and is composed of the following components:

- A solid storage core to contain the deposited solar energy for use during cloud cover conditions.
- A movable insulation shield to control the rate of heat transfer from the core to the working gas.
- A core/shield envelope to aid in core support and to prevent the working gas from coming in contact with the core/shield area.
- An insulation shield retractor and bi-metal, gas expansion or other type of device to allow control of the movable shield to maintain constant outlet gas temperature.
- A bellows to allow shield retraction.
- An inert gas bleed system to provide positive pressure of inert gas in the core/shield container preventing the pressurized working gas from entering the core/shield region.
- Insulation to minimize heat leakage.
- A gas baffle to direct the working gas flow.
- A heat exchanger with tubular gas passages to transfer the storage core heat energy to the working gas.
- A honeycomb heat exchanger to gather solar energy and transfer it directly to the working gas.
- A quartz window to allow concentrated solar energy to be deposited in the receiver.
- A sapphire window to allow some of the solar energy to be deposited on the core surface.
- Reinforcing rods to help support the receiver inner components.
- A steel structural vessel to house and provide mounting for the buffer heat receiver and to contain the working gas.

The latent heat receiver is shown in Figure 2 and is composed of the following components:

- A latent heat storage core (silicon) to retain the deposited solar energy for use during cloud cover conditions.
- A core container material (boron nitride) to contain the molten silicon.
- A graphite frame to house and support the core container.

and, if necessary, to identify optimum size and candidate storage concepts which meet specified cost and weight goals and to develop specific component and subsystem hardware.

Project Efforts.

The task described above comprises both in-house and contracted efforts as shown in Table 1.

TABLE 1. DEVELOPMENT OF LATENT HEAT BUFFER STORAGE

Activity	Effort Mode	Status
Heat Transfer Computer Code	In-house	Completed in FY '80 [Ref. 1]
Buffer Storage Requirements (Stirling and Rankine)	Contracted	Completed in FY '80 [Ref. 2 & 3]
Buffer Storage Requirements (Brayton)	Contracted	Completed in FY '81
PCM Selection Containment	In-house	Completed in FY '80 [Ref. 4]
Advanced Concepts	Contracted	Completed in FY '81 [Ref. 5]
Heat Transfer Enhancement	In-house	Continuing
Material Corrosion Tests	In-house	Continuing
Subsystem Research Experiment (SRE)	Contracted	Postponed Due to Budget Recision
Solidification Control	Contracted	Postponed Due to Budget Recision

Those task activities completed or continuing in FY '81 are briefly described below.

Buffer Storage Requirements (Dish/Brayton).

Garrett-AiResearch has completed the technical effort to identify and assess the thermal buffer storage requirements of the Dish/Brayton System. A companion paper in this meeting describes the effort.

Advanced Concepts.

Hanford Engineering Development Laboratory (HEDL) conceived two separate advanced high temperature buffer storage subsystems suitable for operation at ~1370°C. One concept uses sensible heat storage in solid graphite while another uses storage of latent heat in molten silicon. The receiver integrated design requirements are shown in Table 2.

TABLE 2. BUFFER STORAGE DESIGN REQUIREMENTS SUMMARY

DESIGN CHARACTERISTICS	JPL REQUIREMENTS	HEDL SENSIBLE BUFFER HEAT RECIEVER	HEDL LATENT BUFFER HEAT RECEIVER
Inlet Gas Temperature	950°C	950°C	950°C
Outlet Gas Temperature	1370°C	1370°C	1370°C
Gas Pressure	45 psia	45 psia	45 psia
Maximum Δ Pressure	4%	0.299%	0.06%

- A multipurpose container to aid in support and prevent oxygen interaction with the core components. This container also keeps the silicon upright during sun tracking. The housing is cylindrical shaped with an aperture for solar energy deposition.
- An argon bleed to flush oxygen from the core and prevent oxidation at high temperatures.
- A heat exchanger to transfer the heat energy to the work fluid (air).
- Refractory bearings to allow free movement of the core.
- A support yoke to provide bearing and core component support.
- A refractory cement to minimize heat loss and provide support for all receiver components.
- A steel outer shell to allow for receiver mounting.

Heat Transfer Enhancement Experiments

Objective: The objective of these tests is to check the heat transfer enhancement feature of metal-halide mixture (Na-NaCl) over pure halide itself (NaCl).

Method: The method of the test is to use two heat transfer capsules of identical dimensions and geometries (as shown in Figure 3) to contain identical volumes of pure NaCl and Na-NaCl (Equimolar) mixture, separately, and compare the heat extraction rates of these capsules.

Progress:

- o Two sets of data (at Nitrogen flow rates of 2.5 SCFM and 5 SCFM) have been obtained from heating and cooling of pure NaCl capsules.
- o Four tests (at Nitrogen flow rates 2.5, 5, 10, and 15 SCFM) will be performed on Na-NaCl mixture capsule.
- o Heat extraction rates will be compared.

Material Corrosion Tests.

Containment materials and corrosion experiments are being conducted under thermal cycling conditions to characterize molten-salt corrosion behavior. Both capsule and free convection loop experiments are in progress to obtain realistic corrosion data. The specific experiments are as follows:

1. Capsule Tests.
    a) Salts Being Tested:
        i) 69.8 NaF/MgF_2 in SS, 321 and 430
        ii) 75 NaCl/Na in SS, 321, and 430
        iii) NaCl in 9 Cr, 1 Mo and SS 430
    b) Conditions:
        i) High purity
        ii) High purity + gettering (Zirconium)
        iii) Commerical purity
        iv) Commercial purity + gettering (Zirconium)
    c) Test Times: 2000, 4000 and 8000 hours
    d) Capsule Description:
        i) Total number of capsules = 108

ii) Most capsules contain a tensile sample

iii) Four tensile samples outside the capsules for each time and temperature

iv) Weight changes on tensile sample

v) Vacuum test atmosphere

e) Special Capsules:

i) One commercial purity plus getter capsule will be tested in a tube furnace with Nitrogen flowing as cover gas to obtain rapid temperature cycling. Each of these capsules will be instrumented with a thermowell.

ii) One thermowell capsule will be included in each group of samples to assure full melting and solidification of the test salt.

2. Thermal Circulation Loop Tests.

a) 3 loops

b) Each to be commercial purity salt + getter

c) Test time = 2000 hours

d) Each loop to contian 8 tensile samples, 4 in the hot vertical leg and 4 in the cold vertical leg

Some of the 2000 hour and 4000 hour capsule test corrosion data is shown in Table 3.

TABLE 3. WEIGHT CHANGE (Mg/Cm^2 Total)

Salt System	Containment Alloy	Getter	After 2000 Hr	After 4000 Hr
Na/Pure NaCl	321 SS	None	-8	-232 (Air Leak)
Na/Comm NaCl	"	None	-477 (Air Leak)	-4
Na/Pure NaCl	"	Zr Foil	-0.3	-
Na/Comm NaCl	"	Zr Foil	-303 (Air Leak)	-626 (Air Leak)
Na/Pure NaCl	9 Cr-1 Mo	None	+0.6	+47
Na/Comm NaCl	"	None	+5	+123
Na/Pure NaCl	"	Zr Foil	+0.3	+36
Na/Comm NaCl	"	Zr Foil	-	+86
NaF/MgF$_2$	321 SS	None	-22	+236
NaF/MgF$_2$	"	Zr Foil	-11	+182

Some important observations are:

- Na/NaCl system is less corrosive than Na/MgF$_2$.
- Air/Moisture leakage in either system is disasterous - extreme corrosion.
- 9Cr-1 Mo alloy lacks sufficient strength, air oxidation resistance and corrosion resistance to Na/NaCl for long term application.

- 321 SS has adequate strength and corrosion resistance. Air oxidation resistance is questionable for long term application.

REFERENCES

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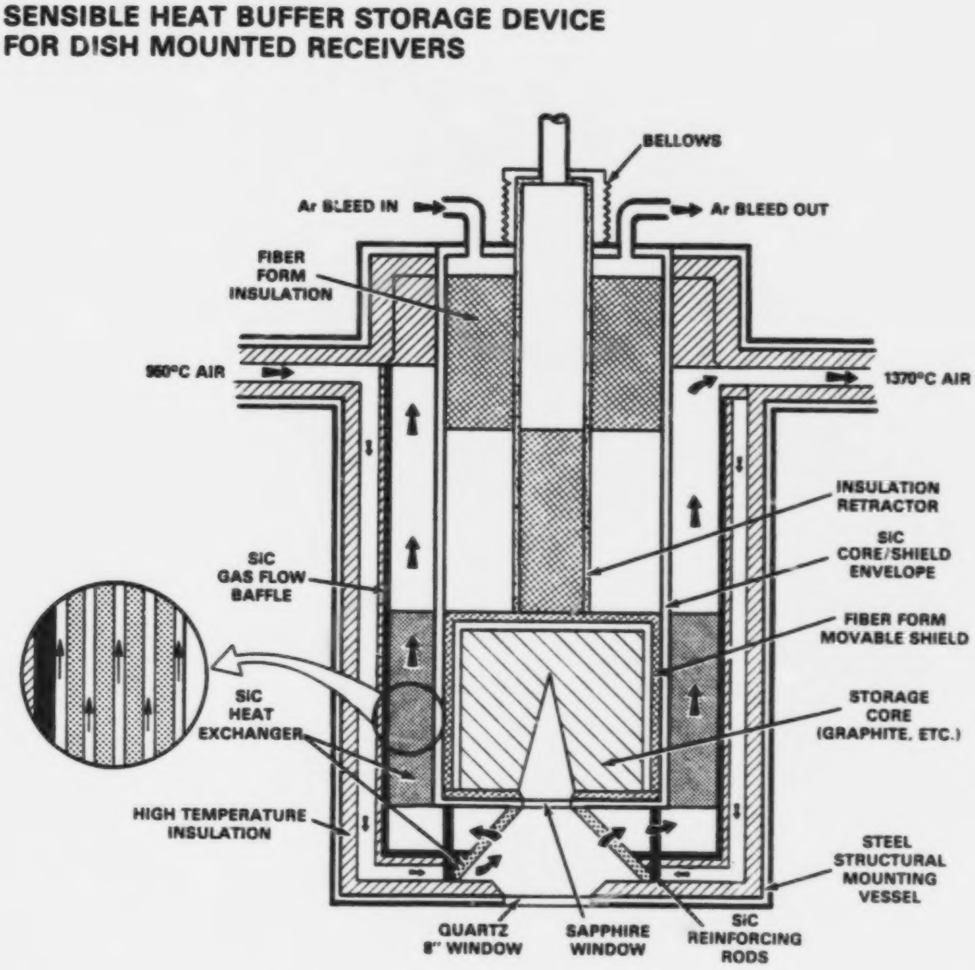

SENSIBLE HEAT BUFFER STORAGE DEVICE FOR DISH MOUNTED RECEIVERS

BELLOWS
Ar BLEED IN
Ar BLEED OUT
FIBER FORM INSULATION
950°C AIR
1370°C AIR
INSULATION RETRACTOR
SIC CORE/SHIELD ENVELOPE
SIC GAS FLOW BAFFLE
FIBER FORM MOVABLE SHIELD
SIC HEAT EXCHANGER
STORAGE CORE (GRAPHITE, ETC.)
HIGH TEMPERATURE INSULATION
STEEL STRUCTURAL MOUNTING VESSEL
QUARTZ 8" WINDOW
SAPPHIRE WINDOW
SIC REINFORCING RODS

Figure 1. Conceptual Design

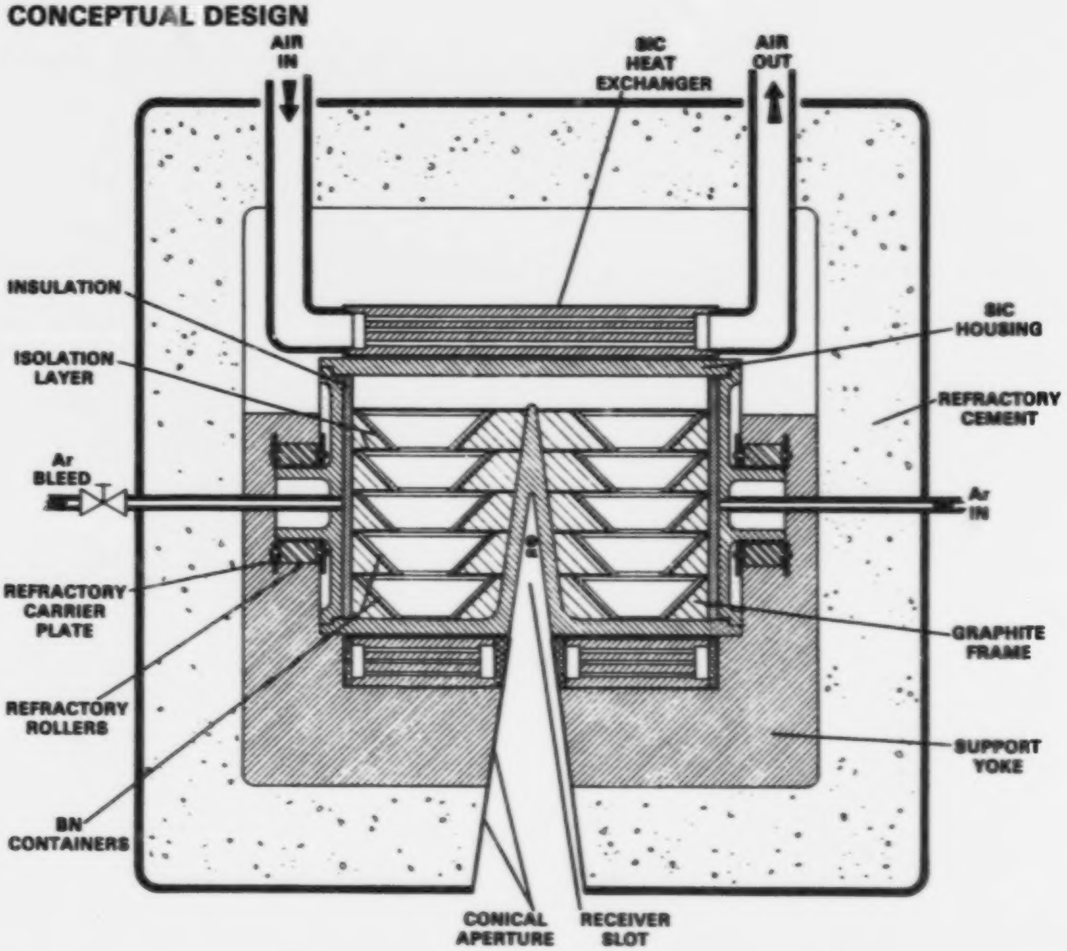
CONCEPTUAL DESIGN
AIR IN
SiC HEAT EXCHANGER
AIR OUT
INSULATION
SiC HOUSING
ISOLATION LAYER
REFRACTORY CEMENT
Ar BLEED
Ar IN
REFRACTORY CARRIER PLATE
GRAPHITE FRAME
REFRACTORY ROLLERS
SUPPORT YOKE
BN CONTAINERS
CONICAL APERTURE
RECEIVER SLOT

Figure 2. Silicon Latent Heat Storage Device

BEST DOCUMENT AVAILABLE

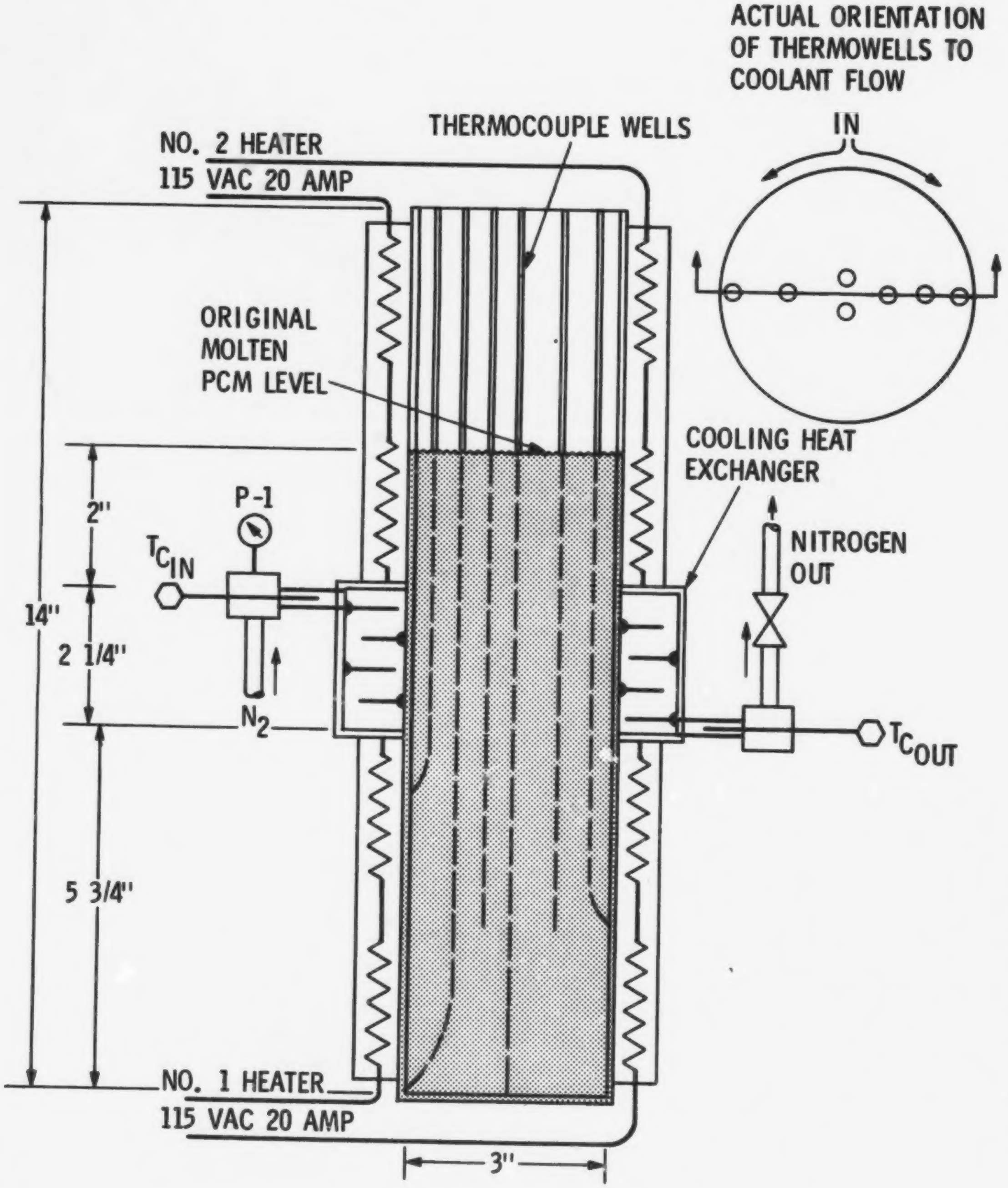
ACTUAL ORIENTATION OF THERMOWELLS TO COOLANT FLOW
IN
THERMOCOUPLE WELLS
NO. 2 HEATER
115 VAC 20 AMP
ORIGINAL MOLTEN PCM LEVEL
COOLING HEAT EXCHANGER
2"
P-1
$T_{C_{IN}}$
NITROGEN OUT
14"
2 1/4"
N_2
$T_{C_{OUT}}$
5 3/4"
NO. 1 HEATER
115 VAC 20 AMP
3"

Figure 3. Two Heat Transfer Capsules

PROJECT SUMMARY

Project Title: Air Brayton Solar Receiver Phase III: Storage Requirements Definition Study

Principal Investigator: Hal J. Strumpf

Organization:
AiResearch Manufacturing Company
A Division of The Garrett Corporation
2525 West 190th Street
Torrance, California 90509

Project Goals: Establish the need, requirements, and size of latent heat buffer thermal energy storage for a typical air Brayton solar receiver.

Project Status: The project has been completed. The final report has been issued as AiResearch Report 81-18087.

To demonstrate the effect of buffer thermal energy storage on engine operation, a computer program was written for complete transient/steady-state Brayton cycle performance. The program models the recuperator, receiver, and thermal storage device as finite-element thermal masses; actual operating or predicted performance data are used for all components, including the rotating equipment.

The solar insolation input is minute-by-minute data recorded at the NASA/JPL test facility at Edwards Air Force Base for the year 1979. Based on this input and a specified control scheme, the computer program predicts the Brayton engine operation, including flows, temperatures, and pressures for the various components, along with the engine output power.

Because computer time considerations made it impractical to model an entire year's operation, a simulated year was developed. This involves grouping days with similar insolation patterns and selecting a representative day from each group. To determine the year's performance, the results from each of the representative days are multiplied by the number of days in the group, and all these products summed and normalized.

Simulated years were run for various weights of sodium chloride and lithium carbonate phase-change materials. The results indicate that thermal storage can afford a significant decrease in the number of engine shutdowns as compared to operating without thermal storage. It has also been found that the number of shutdowns does not continuously decrease as the storage material weight increases. In fact, there appears to be an optimum weight for minimizing the number of shutdowns. This is because of the sensible heat effects of the storage material. A large weight will not increase in temperature as rapidly as a small weight, given the same thermal input. This could result in lower cycle temperatures during a solar outage and cause an engine shutdown. Of course, too small a weight limits the storage capacity and increases the number of shutdowns.

An economic parametric study was performed to compare the cost of a thermal storage device with the savings in engine replacement afforded by the thermal storage. The study indicates that the economic viability of buffer thermal energy storage is largely a function of the achievable engine life. At low predicted life, thermal storage is economically attractive; for highly reliable, long-lived engines, thermal storage is not economical.

Contract Number: NAS 7-100/955136

Contract Period: November 1, 1980 through June 30, 1981

Funding Level: $50,000

Funding Source: Sandia National Laboratory through the Jet Propulsion Laboratory

APPLICATION OF BUFFER THERMAL ENERGY STORAGE TO AN AIR BRAYTON SOLAR ENGINE

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ABSTRACT

This paper summarizes the results of a study on the application of latent-heat buffer thermal energy (TES) storage to a point-focusing solar receiver equipped with an air Brayton engine. The AiResearch 85-kw(th) Air Brayton Solar Receiver (ABSR) and Mod "O" engine were used as a baseline system.

The operating life of a Brayton engine depends, in general, upon the number of start-stop cycles. The main advantage of buffer thermal energy storage is that it enables the engine to continue running during periods of cloud cover, thus reducing the number of engine shutdowns and increasing engine life.

To demonstrate the effect of buffer thermal energy storage on engine operation, a computer program was written for complete transient/steady-state Brayton cycle performance. The solar insolation input was minute-by-minute data recorded at the NASA/JPL test facility at Edwards Air Force Base for the year 1979.

The results of the study indicated that thermal storage can afford a significant decrease in the number of engine shutdowns as compared to operating without thermal storage. It has also been found that the number of shutdowns does not continuously decrease as the storage material weight increases. In fact, there appears to be an optimum weight for minimizing the number of shutdowns.

The study also indicated that the economic viability of buffer thermal energy storage is largely a function of the achievable engine life. At low predicted life, thermal storage is economically attractive; for highly reliable, long-lived engines, thermal storage is not economical.

INTRODUCTION

A study has been conducted on the application of latent-heat buffer thermal energy storage to a point-focusing solar receiver equipped with an air Brayton engine. The main goal of the study was to establish the need, requirements, and size of buffer storage for a typical Brayton engine. Buffer storage is, by definition, of relatively low capacity, sufficient for keeping the engine running during brief periods of cloud cover (solar outages) but insufficient for long durations of low solar insolation.

The AiResearch 85-kw(th) ABSR and Mod "O" engine were used as the baseline system. The engine consists of a compressor, turbine, generator, and recuperator. The cycle is shown schematically in Fig. 1. As can be seen, the cycle is "open"--ambient air is ingested by the compressor, picks up heat from the exhaust stream in the recuperator, absorbs the solar input in the receiver, is expanded in the turbine (producing the engine's power), and gives up heat to the incoming air before being exhausted to the environment. The thermal storage device (TSD) is also shown in Fig. 1. The version of the Mod "O" engine used for the present study does not contain an auxiliary combustor for hybrid operation.

Depending upon the Brayton cycle pressure ratios and efficiencies, there is a minimum working fluid air temperature that must be supplied to the turbine to maintain cycle operation. During periods of solar outage, the primary heat source is removed or limited. The working fluid will initially extract heat from the thermal capacitance of the receiver and recuperator; but, after a time, energy must be supplied from an auxiliary source if the engine is to remain running.

A latent heat of fusion buffer TSD is the auxiliary source investigated in this study. Energy is supplied to the cycle air from the latent heat released by the solidification of a phase-change material (PCM), which, in the temperature range of interest, will be an inorganic salt.

The main advantage of buffer TES is its ability to reduce the number of start-stop cycles required of the Brayton engine. For operation in a positive-net-power, self-sustaining mode, the power produced by the turbine must be greater than the power consumed by the compressor. This condition requires a reasonably high turbine inlet temperature (TIT). The thermal capacitance of the receiver, recuperator, and ducting is sufficient to maintain the necessary TIT for only a few minutes during a solar outage. The addition of thermal storage substantially increases the thermal capacitance of the system, resulting in an extension of the periods of solar outage during which the engine can remain running. Because many solar outages are of short duration, buffer TES can substantially reduce the number of engine shutdowns. With the operating life of the engine used in this application largely a function of the number of start-stop cycles, TES has the potential for increasing engine life and, hence, reducing engine yearly cost. Balanced against this is the cost of the TSD and its required auxiliary equipment. Depending upon the mode of system operation, the TSD may or may not result in an increase in the electrical energy produced. Any increase is likely to be small and will not, in itself, establish the desirability of buffer thermal storage.

To demonstrate the effect of buffer TES on engine operation, a complete transient Brayton cycle performance computer program was written. The program models the recuperator, receiver, and TSD as finite-element thermal masses; all components, including the rotating equipment, utilize actual operating or predicted performance data.

SOLAR INSOLATION

For an analysis of the effect of buffer TES, the solar insolation distribution must be input. Actual minute-by-minute insolation data were obtained from JPL for the NASA/JPL test facility at Edwards Air Force Base, California, for the entire year of 1979.

Because weather and solar insolation conditions vary over a year, a full year should be considered when analyzing the overall effect of TES. However, running 365 days on a transient computer program was considered excessively costly, especially when a number of years were to be run for various thermal storage conditions. Therefore, the concept of a simulated year was developed. Review of the data indicated that there were days with similar insolation patterns. For example, certain days had moderate clouds in the morning and were clear in the afternoon; other days were totally clear; etc. Days with similar insolation patterns were combined into groups, and a representative day selected from each group. A total of eleven groupings was formed. To determine the year's performance, each representative day is run on the developed transient computer program, with the results from each day multiplied by the number of days in the group, and all these products summed.

The net heat input to the fluid in the receiver is assumed to be proportional to the solar insolation. The baseline conditions are a gross heat input of 85 kw(th) at an insolation value of 1000 w/sq m. At a cavity efficiency of 85 percent, this is equivalent to a net heat input of 72.25 kw(th). Thus, for any value of solar insolation, Q, the net heat input to the fluid is taken as 72.25 x Q/1000 kw(th).

SOLAR BRAYTON ENGINE COMPUTER PROGRAM

The computer program developed to analyze the air Brayton solar engine is a transient/steady-state performance program that predicts the time-dependent behavior of the modeled system in response to the initial and boundary conditions. The model contains control elements that modify system behavior according to the control logic and the values of certain performance indicators.

Two important points about the modeling are (1) that proper consideration has been given to the thermal capacity of the massive system components and to their effects on system time response and (2) that realistic performance specifications have been used for both the heat transfer components and the rotating equipment. The recuperator, receiver, and TSD are each modeled using finite elements. The temperature change at each node during a time increment is calculated as a function of the local temperature gradients and the strengths of the various thermal couplings between the node in question and its neighboring nodes.

The system relationships form a set of nonlinear simultaneous equations that are solved through the use of a multidimensional Newton technique. This is an iterative method that involves a series of successive linearizations. The development and solution of the system equations are described in reference 1.

The finite element models are similar for the recuperator and receiver; the major difference accounts for the fact that the receiver is a one-fluid heat exchanger whereas the recuperator is a two-fluid heat exchanger. The TSD model is also similar, i.e., a fluid (air) in contact with massive elements (PCM). However, the treatment of the massive elements is quite different for the TSD. The massive elements for the recuperator and receiver represent the metallic walls of the heat exchanger. The resistance to heat transfer of these walls is quite low and can be safely neglected. For the TSD, however, the massive PCM can represent a significant resistance to heat transfer and must be considered.

The PCM can be completely solid, completely liquid, or in the two-phase regime in the melting or freezing mode. The resistance calculation is different for each of these conditions. It should be noted that each PCM element is considered a separate entity; i.e., each has its own temperature and phase boundary location. To account for the most general TSD design, longitudinal conduction between adjacent PCM elements is not included.

For PCM completely solid, the resistance is a function of the PCM solid thermal conductivity and the thickness of the PCM layer. For PCM in the freezing mode, the resistance is a function of the PCM solid thermal conductivity and the thickness of the solid PCM, i.e., the distance between the cycle fluid and the PCM phase boundary. For PCM completely liquid or in the melting mode, the conductive resistance is related to the PCM liquid thermal conductivity and the appropriate thickness. However, heat can also be transferred through the PCM layer by natural convection; this additional contribution to the heat transfer is included in the calculations. Further details of the component modeling can be found in reference 1.

COMPONENT SPECIFICATIONS

Realistic performance specifications have been used with the computer program for the recuperator, receiver, and rotating equipment. The heat exchanger convective coupling strengths (thermal conductances) were determined from calculations of component performance over a range of flows and termperatures. The calculations were based on AiResearch experience with the heat transfer characteristics of the surfaces used for the components. The pressure drops were taken as 3 percent of the inlet pressure for the recuperator hot side, 1 percent of the inlet pressure for the recuperator cold side, and 3 percent of the inlet pressure for the receiver. The operating characteristics of the rotating equipment were taken from actual performance maps of the Mod "0" turbine and compressor.

In accordance with usual practice, some of the flow from the compressor outlet (taken as 2 percent) is used to cool the bearings. This flow is assumed to be added to the turbine exit flow. Thus, the turbine flow is always taken as 2 percent less than the compressor flow.

The TSD is the one major component in the Brayton engine that does not have an existing design. The study effort involved varying the PCM material and weight to determine the effect on performance; thus, the TSD component specification changes for each run.

Although the TSD model is completely general, a particular configuration must be assumed to determine the specifications required to run the computer program. Different configurations with the same characteristics (fluid thermal conductance, PCM resistance, weight of PCM, etc.) will perform similarly, so the selection of a design is not critical. The representative configuration selected is that of a shell and tube heat exchanger. The unit consists of a bundle of hollow tubes through which the cycle fluid (air) flows. Surrounding the tubes, and filling up the shell, is the PCM. The configuration is shown schematically in Fig. 2. As indicated in Fig. 2, there are two tube-side passes. The two-pass design is well suited to the orientation variations that would be encountered by a TSD mounted in the engine plane. With a single-pass design, if the tubes are in a near-horizontal orientation, some of the tubes may not be surrounded by PCM when the PCM is in the solid phase. This is because of the difference in density of the liquid and solid phases of the PCM (as much as 25 percent). Volume must be available to handle the entire PCM weight at its highest liquid temperature. Thus, in the solid phase, substantial tube surface might not be covered with PCM. This could result in complete bypassing of some of the cycle air, resulting in a loss of heat exchanger effectiveness because there would be no heat transfer to these tubes. The two-pass design ensures that complete bypassing cannot occur regardless of heat exchanger orientation; all the tubes in one of the passes would always be covered.

For this general configuration, the thermal conductances are calculated using conventional round tube heat transfer relationships. The PCM resistance calculations have been previously discussed. For all TSD sizes studied, the tube configuration was adjusted to yield an air-side pressure drop of 2 percent of the inlet pressure for full flow through the unit. At reduced flows, the pressure drop was reduced proportionately.

SYSTEM OPERATION

As can be seen from the schematic in Fig. 1, the TSD is located downstream of the receiver and upstream of the turbine. Also shown is a valve that enables some or all of the flow through the receiver to bypass the TSD and go directly to the turbine. This flow control valve is an expensive piece of equipment, requiring three-way flow modulation, high temperature operation (up to 1500°F), and relatively large size (a 4-in. valve is necessary to limit pressure losses). Nevertheless, the valve is considered to be a necessary component. Removal of the valve would require the TSD to be in line with the receiver and turbine at all times. This presents an unacceptable penalty during a cold startup, when the entire engine (including the TSD) has to be heated to operating temperature from ambient or near ambient conditions. During such a startup the attainment of a self-sustaining TIT would be delayed while the TSD is heated. Motoring times of around 45 min would be required. This is considered to be excessive for the Mod "0" engine. In addition to the long motoring time, a large energy storage capacity would have to be made available through storage batteries or similar devices.

The flow control valve is used to modulate the flow rate through the TSD as a function of air temperature. The valve positions are illustrated in Fig. 3: part a of the figure shows a complete bypassing of the TSD, part b shows a partial flow through the device, and part c shows full flow with the TSD in series with the receiver. The position of the modulating valve and, hence, the flow rate through the TSD, is determined by simple control logic keyed to a control temperature (TC). This logic, and its integration into the system operation, is described below.

The operating conditions for the engine were selected after some preliminary study as representative of a reasonable operating approach. Three cycle air temperature measurements are required, as indicated in Fig. 3: receiver outlet temperature, T15; TSD outlet temperature, T16; and TIT, T8. No temperature measurements are required in the PCM. Also required is a solar pyraheliometer to measure the local value of the solar insolation.

The measured temperatures control the position of the modulating valve and the speed of the rotating group. By the use of guide vanes and restricting orifices, the turbomachinery can be controlled to yield any set temperature in the system or to rotate at a given speed. A control box is required to orchestrate these functions. The control scheme is expected to be readily transferable to a real engine.

At the start of each day, all components are assumed to be at ambient temperature (70°F). This is a conservative approach, because on some days temperatures may be somewhat above ambient (especially in the TSD). As will be discussed below, the system (including the TSD) is allowed to run itself down at the end of each day, so the components are relatively cool at shutdown. The approximate average component temperatures at shutdown are: recuperator, 500°F; receiver, 630°F; and TSD, 800°F.

The mirror is assumed to be defocused at the beginning of the day, and remains so until the solar insolation reaches a minimum value, taken as 450 w/sq m. This value is sufficient for self-sustained engine operation at a power output of around 4 kw and a cold startup motoring time of about 20 min, about the maximum desirable for the Mod "0" engine. Lower values of the startup insolation might result in excessive motoring times (if self-sustained operation can be attained at all). Higher values tend to waste some of the available solar energy.

As the mirror is focused, the rotating group is turned on, using an auxiliary power supply to motor the engine at 53,000 rpm. The engine must be running any time the mirror is focused, to prevent rapid overheating of the receiver. The fluid flow completely bypasses the TSD, as shown in Fig. 3a. If during this motoring period the insolation drops below 400 w/sq m, the engine is shut off and the mirror defocused. This is done to prevent useless motoring and draining of the auxiliary power supply. The mirror is focused and the engine restarted when the insolation again reaches 450 w/sq m.

As the components heat up, the cycle air temperature increases until a net positive power is produced by the engine. This occurs at a TIT of around 800°F. At this point, the auxiliary power supply is disconnected. The engine continues to run with the rotating speed controlled at 53,000 rpm. Once the positive net power condition is attained, the engine is allowed to run until it shuts itself down; thus insolations below 400 w/sq m do not result in automatic shutdown. Any shutdown is accompanied by mirror defocusing. The engine is always restarted (and the mirror focused) when the insolation reaches 450 w/sq m. During temporary shutdowns, the recuperator, receiver, and TSD temperatures are assumed to be unchanged. This is a reasonable assumption because, with good insulation, shutdown durations of less than a half-hour will not result in much temperature change. Thus, once positive net power has been attained, any subsequent restarts on that day will require only an initial burst of power from the auxilary source, because the fluid temperature conditions will almost immediately be self-sustaining.

As the engine runs and the solar insolation increases, the receiver and recuperator temperatures increase until the TIT (T8 in Fig. 3) reaches the control temperature, TC. At this point, partial flow is initiated through the TSD (Fig. 3b). To limit the required flow range of the modulating valve, a minimum TSD flow equal to 10 percent of the receiver flow is assumed. This flow will immediately lower the TIT, so the TC should be chosen high enough that the engine will not turn off at this point. When the TIT again becomes equal to the TC, the flow rate through the TSD is increased so as to maintain this equality.

As the system continues to heat up, the TSD outlet temperature (T16) reaches the TC. At this point, all the receiver flow will be going through the TSD (Fig. 3c). Further heating results in the TIT exceeding the TC. The engine has been running at 53,000 rpm all this time. When the receiver outlet temperature (T15) reaches 1500°F, the cycle control is switched so as to maintain this temperature; the speed is allowed to vary to effect this control. It should be noted that the receiver outlet temperature rather than the TIT is controlled. This protects the receiver from possible high temperatures because with the TSD in series (Fig. 3c) a T8 of 1500°F could be accompanied by a considerably higher T15. The 1500°F air temperature limit is the design maximum for the ABSR.

As the insolation increases, the fluid flow rate (and hence, the engine speed) must increase so as not to exceed a 1500°F outlet temperature. Conversely, the speed decreases as the insolation drops. If the speed drops to as low as 53,000 rpm, this value is maintained and the temperature is no longer controlled. This minimum speed was selected to limit the recuperator hot-side inlet temperature to about 1200°F, the nominal limit for the Mod "0" design. Maintaining a TIT of 1500°F at speeds less than 53,000 rpm will result in excessive recuperator temperatures.

A continuing decrease in insolation will eventually result in T8 dropping below the TC. However, since T16 will be greater than T15, full flow is maintained through the TSD. The system continues in this mode until it shuts itself down. Any subsequent startups will occur with T16 greater than T15, so the full flow is routed through the TSD (Fig. 3c).

Other control strategies are possible. For example, rather than controlling speed at lower levels of insolation, the TIT could be maintained at a value low enough to protect the recuperator. Also, the cold startup speed might possibly be reduced, because the temperatures are low during this phase. The turbine efficiency, however, tends to decrease at lower speeds. In addition, the lower speeds may result in mismatched conditions between the turbine and compressor, preventing a smooth startup.

A quite different flow scheme was considered and some sample runs made. The approach used low-level insolation (less than 450 w/sq m) at the beginning of the day to partially heat the TSD. Because it is not desirable to motor the engine excessively, an auxiliary flow loop was employed, using a separate compressor or fan to flow air through the receiver and TSD without running the engine. It appears that this approach has the potential to decrease the number of engine shutdowns while increasing the net energy produced. Also the engine startup power required is substantially reduced. However, in addition to the extra compressor, a number of three-way valves, including at least one expensive 1500°F valve, would be required. In addition, the energy required to operate the auxiliary compressor would have to be stored, requiring a large increase in storage battery capacity. It is felt that despite the potential advantages, the increased complexity and cost of this approach renders it impractical.

BRAYTON ENGINE PERFORMANCE

Simulated years were run for six combinations of thermal storage materials, weights, and control temperatures. Two PCM's were studied: NaCl (melting point = 1472°F) and Li_2CO_3 (melting point = 1333°F). A summary of the results is given in Table 1. The net energy is the yearly energy output minus twice the yearly energy input. The factor of two represents a 50-percent in-to-out efficiency for charging and discharging an electrical energy storage device (such as a battery).

All but one of the simulated years were for a TC of 1000°F. As previously discussed, from a cold startup this temperature must be attained at the receiver outlet before any flow is routed through the TSD (see Fig. 3). Subsequently, the turbine inlet temperature is controlled to this value until the TSD is heated sufficiently to allow the TIT to rise with full flow passing through the TSD. The 1000°F TC is about as low as is possible without causing a shutdown when the TSD flow is first initiated (and the TIT drops considerably from the TC). The one run at a higher TC (1300°F) did not result in improved performance; the slightly increased energy output was more than offset by an additional 100 shutdowns.

The simulated-year results in Table 1 indicate that thermal storage can produce a significant decrease in the number of shutdowns as compared to a system with no thermal storage (a 40-percent decrease in the case of 200 lb of NaCl at TC = 1000°F). Whether this decrease, and the accompanying increase in engine life, is sufficient to pay for the thermal storage system will be discussed in the Economic Analysis Section.

From the first four entries in Table 1, it can be seen that the number of shutdowns does not continue to decrease as the PCM weight increases. This is because of the sensible heat effects of the PCM. The charging and discharging of the TSD involves a significant amount of sensible heating and cooling; indeed, the PCM is at ambient conditions at the start of a day, and the heat required to raise the temperature to the melting point is considerably greater than the latent heat for either PCM. A large PCM weight will not increase in temperature as rapidly as a small weight, given the same thermal input.

This could result in a lower turbine inlet temperature during a solar outage and cause an engine shutdown. Of course, too small a PCM weight limits the storage capacity and may decrease the length of time the engine can remain running with reduced solar insolation.

A similar effect is noticeable when comparing equal weights of NaCl and Li_2CO_3. The Li_2CO_3 has a solid heat capacity roughly two and one-half times that of the NaCl, so the Li_2CO_3 will not heat up as rapidly. This results in an increase in the number of shutdowns.

To further investigate this trend, additional runs were made for a single day, using the solar insolation data for April 7, 1979, a heavily clouded day. These results are presented in Table 2. All runs were at TC = 1000°F.

Table 1

Simulated-Year Thermal Storage Summary

PCM	PCM Weight, lb	Control Temperature, °F	Number of Shutdowns	Net Energy, kwhr
--	0	--	1,810	44,676
NaCl	100	1,000	1,202	41,983
NaCl	200	1,000	1,084	40,723
NaCl	400	1,000	1,318	38,310
NaCl	200	1,300	1,188	41,276
Li_2CO_3	200	1,000	1,276	37,138

Table 2

Thermal Storage Summary For April 7, 1979

PCM	PCM Weight, lb	Number of Shutdowns	Net Energy, kwhr
--	0	14	44.9
NaCl	100	11	38.0
NaCl	200	8	34.0
NaCl	400	11	25.4
Li_2CO_3	50	9	37.3
Li_2CO_3	100	8	32.2
Li_2CO_3	200	9	25.0

It can perhaps be generalized from the results in Tables 1 and 2 that for given solar input conditions, any potential thermal storage PCM would have an optimum weight for minimizing the number of shutdowns: this interesting conclusion has not been apparent prior to the present work. Indeed, it was generally assumed that thermal storage performance improved as the PCM weight was increased.

On the other hand, the trend in net energy produced seems to be more straightforward: the energy decreases with increasing PCM weight. This is because it is assumed that the TSD cools to ambient temperature before the start of each day. Since the TSD shutdown temperature is about 800°F, a substantial amount of energy is lost each day, especially for a high heat capacity material such as Li_2CO_3. The additional energy produced as a result of the reduction in number of shutdowns is small, not nearly enough to overcome the TSD environmental losses.

Fig. 4 presents computer-generated plots of some of the data for the 200-lb- NaCl TSD for April 7. The solar insolution input, along with two of the key outputs, TIT and TSD outlet temperature, are shown. From the plots, the engine operating characteristics can be observed. It should be noted that during shutdown periods, the fluid temperatures are constant. This reflects the assumption of negligible thermal losses. When the engine is first turned on, all the flow bypasses the TSD. When the TIT reaches the TC (at about 8.5 hr), flow is initiated through the TSD. This causes an immediate decrease in the TIT. It should be noted that there have already been two engine shutdowns to this point. As the TSD heats up, the TIT is controlled at 1460°R (1000°F). After the TSD reaches the TC (at about 9.5 hr), the TIT is allowed to increase. At this point, and for the rest of the day, the receiver and TSD are completely in series; i.e., full flow passes through the TSD. For the remainder of the day, the TSD can be observed to be heated and cooled as the solar insolation varies. Shutdown periods are observable as periods of constant TIT and TSD outlet temperature. It is significant to note that the TSD operates almost entirely in the sensible heat (solid PCM) regime during the day. There were a total of 8 engine shutdowns with the thermal storage; without thermal storage there were 14 shutdowns.

As a comparison, Fig. 5 presents plots for the 200-lb-NaCl TSD for a clear day, April 20, 1979. It can be seen that during the day the TSD operates primarily in the latent-heat (two-phase PCM) regime.

ECONOMIC ANALYSIS

Incorporation of buffer thermal storage in the solar Brayton engine has been shown to decrease the number of engine shutdowns and, hence, increase engine life. This additional engine life is, of course, offset by the increased initial cost attributable to the TSD and associated hardware. The economic analysis presents a tradeoff of these costs and savings in an effort to determine the economic viability of thermal storage.

In general, achieved engine life is a function of the number of start-stop cycles and the total number of operating hours. This makes it especially difficult to predict engine life for new applications, given the scant data available for engines of this type. It has thus been decided to treat engine life parametrically, rather than make a prediction, in this economic study. To simplify the investigation, engine life has been assumed to be relatively insensitive to operating hours; it will be treated only as function of the number of start-stop cycles.

Engine cost, on the other hand, has been investigated for this application. By scaling cost information for a 10-kw(e) subatmospheric engine, Fortgang and Mayers of JPL have determined required selling prices for a 20-kw(e) solar Brayton engine for various annual production volumes (reference 2). This is essentially equivalent to the Mod "O" engine used for the present study. Fortgang and Mayers determined a selling price of $5328 for the engine at a production rate of 1000 units per year (the lowest production rate studied). This value is used in the present study. It is assumed that the entire engine replacement cost of $5328 must be met at engine failure. In actuality, some engine repair may be possible for certain types of failures; this uncertain situation is not considered.

The life of the TSD is not likely to be cycle-dependent. The large thermal inertia of the device results in only moderate transient effects. Long-term creep and interaction with the molten PCM will make the TSD life largely a function of service life. The TSD replacement cost, which is treated parametrically, is assumed to be completely met at TSD failure.

In addition to the TSD itself, other costs are associated with the thermal storage system. The major item is the high-temperature three-way valve, but there are additional piping, control, and support costs. These are approximated by a fixed cost of $10,000. This is a one-time investment and does not have to be repeated over the 30-yr design life of the power plant.

There is also an energy production penalty associated with using thermal storage (see Table 1). This will be assigned a value of 80 mills/kwhr.

The results of the parametric calculations are presented in Fig. 6, which shows the break-even TSD cost as a function of TSD and engine life. The calculations were performed in such a manner that they could be readily repeated using other cost assumptions and information. The TSD with 200 lb of NaCl was used in the calculations since this design yielded the minimum number of shutdowns. From Table 1 it can be seen that the number of yearly cycles for the engine is 1084 with thermal storage and 1810 without thermal storage. Since the engine cost is $5328, the cost per year is given by:

$\$5328/(N/1084)$ with thermal storage

and

$\$5328/(N/1810)$ without thermal storage

where N is the cycle life of the engine

The energy differential is 44676 - 40723 = 3953 kwhr, equivalent to $316.24/yr if the cost is 80 mills/kwhr. The fixed cost per year for TES is 10,000/30 = $333.33/yr.

The savings per year afforded by the thermal storage is given by:

$$5328/(N/1810) - 5328/(N/1084) - 316.24 - 333.33$$

The break-even TSD cost is the savings per year multiplied by the life of the TSD.

Examination of Fig. 6 indicates that the economic viability of buffer TES is largely a function of achievable engine life. At low predicted life, TES is economically attractive; at greater engine life, TES is less attractive. Indeed, if the engine life is greater than about 6000 cycles, the TSD is not profitable at any cost, because the engine cost savings are balanced by the fixed cost and energy differential.

It should be pointed out that certain costs associated with replacing an engine have not been considered. These include the labor costs and the value of the energy lost during power plant downtime. Inclusion of these costs would tend to improve the economic position of TES. The same general conclusion still applies however—attainment of high engine reliabilties precludes the advantage of buffer thermal energy storage. For less reliable engines, thermal storage may be a cost-saving approach.

REFERENCES

1. Strumpf H. J., and K. P. Barr, Buffer Thermal Energy Storage for an Air Brayton Solar Engine, AiResearch Report 81-18087, August 1981.

2. Fortgang H. R., and H. F. Mayers, "Cost and Price Estimate of Brayton and Stirling Engines in Selected Production Volumes," JPL Publication 80-42, May 1980.

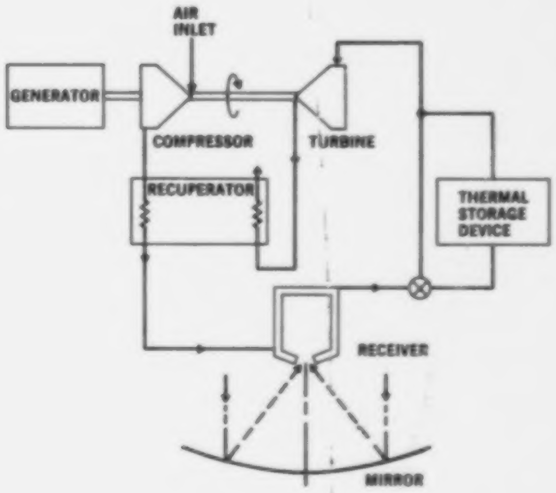

AIR INLET
GENERATOR
COMPRESSOR
TURBINE
RECUPERATOR
THERMAL STORAGE DEVICE
RECEIVER
MIRROR

Fig. 1. Air Brayton Solar Engine Schematic.

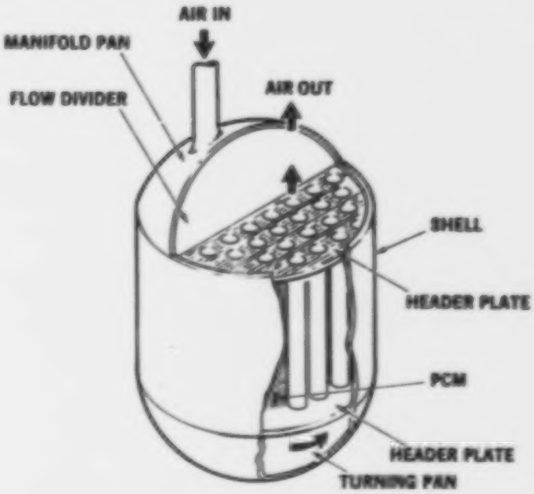
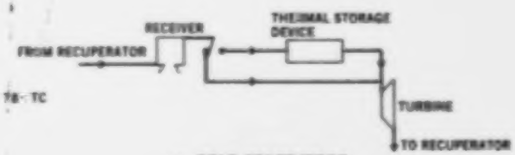
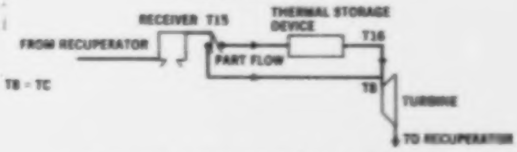

AIR IN
MANIFOLD PAN
AIR OUT
FLOW DIVIDER
SHELL
HEADER PLATE
PCM
HEADER PLATE
TURNING PAN

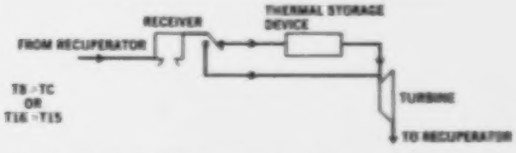
Fig. 2. Thermal Storage Device Configuration.


RECEIVER
THERMAL STORAGE DEVICE
FROM RECUPERATOR
T8 < TC
TURBINE
TO RECUPERATOR

a. COLD-START MODE


RECEIVER T15
THERMAL STORAGE DEVICE
T16
FROM RECUPERATOR
PART FLOW
T8 = TC
T8
TURBINE
TO RECUPERATOR

b. THERMAL STORAGE PARTIAL-FLOW MODE


RECEIVER
THERMAL STORAGE DEVICE
FROM RECUPERATOR
T8 > TC
OR
T16 > T15
TURBINE
TO RECUPERATOR

c. THERMAL STORAGE DISCHARGE OR HIGH-TEMPERATURE MODE

Fig. 3. Thermal Storage and Receiver Flow Scheme.

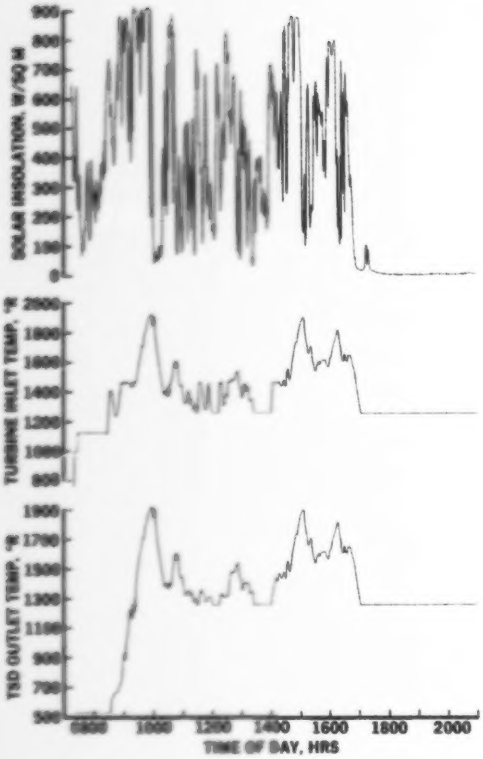


Fig. 4. Computer Plots of 200-lb-NaCl TSD Data (April 7, 1979).

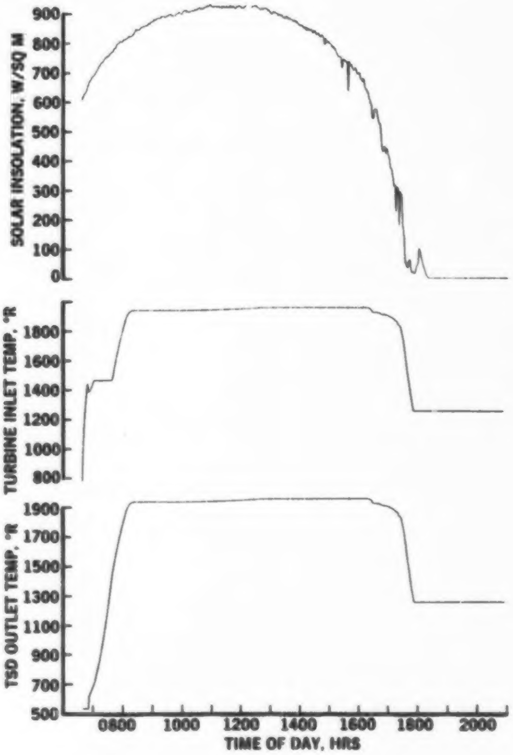


Fig. 5. Computer Plots of 200-lb-NaCl TSD Data (April 20, 1979).

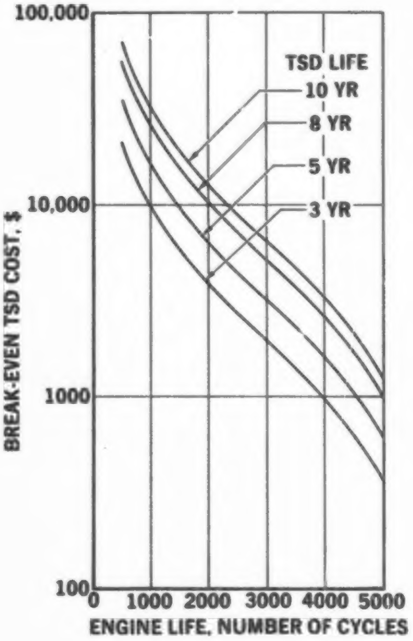


Fig. 6. Break-even Cost for a 200-lb-NaCl TSD.

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SERI - RESEARCH DEVELOPMENT AND ANALYSIS & ASSESSMENTS

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PROJECT SUMMARY

Project Title: The SERI Solar Energy Storage Program

Principal Investigator: Charles E. Wyman

Organization: Solar Energy Research Institute
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Golden, Colorado 80401
(303) 231-1753

Project Goals: The overall objective of this program is to gain a better understanding of advanced thermal energy storage and transport technologies and obtain information that allows developers to select the most promising thermal energy storage technologies; the emphasis of the program is on thermal energy storage for solar thermal power and process heat applications and on thermal energy transport. Research is performed on direct contact heat exchange and thermochemical storage and transport to provide a basis from which to assess these promising technologies. Studies are subcontracted to define new thermal energy storage concepts. Research is also supported to improve the cost and performance of thermal energy transport concepts. Systems analyses identify thermal energy storage concepts for solar thermal applications.

Project Status: Experiments have been performed for direct contact heat exchange and a promising distributor identified. A detailed analysis has been made of the economic and technical potential of thermochemical storage and transport. Rankings have been completed of thermal storage for water/steam, gas-cooled, and organic fluid receiver systems. Grumman Aerospace is continuing a study of a high temperature direct-contact thermal storage system. The University of Washington and IGT are beginning research on new thermal energy storage concepts. Internal insulation of pipelines is being studied as a means to lower thermal transport costs.

Contract Numbers: EG-77-C-01-4042

Contract Period: October 1980-September 1981

Funding Level: $1,050,000

Funding Source: Department of Energy Division of Energy Storage Technology.

THE SERI SOLAR ENERGY STORAGE PROGRAM

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Solar Energy Research Institute
1617 Cole Boulevard
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ABSTRACT

The SERI Solar Energy Storage Program is summarized. The program provides research, systems analyses, and assessments of thermal energy storage and transport in support of the Thermal Energy Storage Program of the DOE Division of Energy Storage Technology; emphasis is on thermal energy storage for solar thermal power and process heat applications and on thermal energy transport. Currently, research is in progress on direct-contact thermal energy storage and thermochemical energy storage and transport. In addition, SERI is directing the definition of new concepts for thermal energy storage and supporting research on thermal energy transport by sensible and latent heat media. SERI is performing systems analyses of thermal energy storage for solar thermal applications and coordinating thermal energy storage activities for solar applications.

INTRODUCTION

As part of the Thermal Energy Storage Program of the DOE Division of Energy Storage Technology, thermal energy storage technologies are developed for identified application areas by the laboratories assigned the lead responsibilities. The SERI Solar Energy Storage Program supports the DOE program by researching thermal storage and transport technologies and by performing analyses and assessments of thermal storage for solar thermal power and process heat applications. Research, analyses, and assessments are also conducted for thermal energy transport systems (Fig. 1).

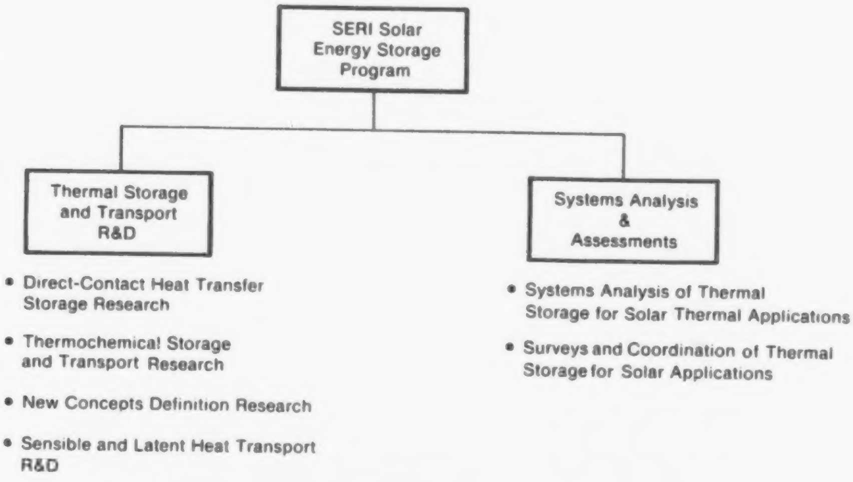
SERI Solar Energy Storage Program
Thermal Storage and Transport R&D
Systems Analysis & Assessments
• Direct-Contact Heat Transfer Storage Research
• Thermochemical Storage and Transport Research
• New Concepts Definition Research
• Sensible and Latent Heat Transport R&D
• Systems Analysis of Thermal Storage for Solar Thermal Applications
• Surveys and Coordination of Thermal Storage for Solar Applications

Figure 1. The FY 1981 SERI Solar Energy Storage Program

The objectives of the SERI Solar Energy Storage Program are to develop a better understanding of thermal energy storage and transport technologies and to obtain information that allows designers to select promising thermal storage and transport technologies for specific applications. We research thermal energy storage options to resolve technical and economic uncertainties that hinder their development. For example, SERI is investigating the storage and transport of thermal energy in chemical bonds (thermochemical energy storage and transport) and studying direct contact between immiscible fluids for latent heat storage. SERI also supports research on innovative thermal energy storage and transport concepts as part of this effort. SERI conducts systems analyses for defined applications to determine thermal storage requirements and to aid in selecting thermal storage technologies. Surveys and assessments also are performed to examine the matches of thermal energy storage technologies with applications. Figure 1 lists the activities now included in the SERI Solar Energy Storage Program.

For FY 1981, the emphasis of these activities is to support the joint plan of the DOE Division of Energy Storage Technology and the Division of Solar Thermal Energy Systems for developing thermal energy storage for solar thermal applications (described in reference 1). The SERI FY 1981 solar energy storage activities are discussed briefly in the following narrative; several of the areas are presented in more detail in other papers at this meeting.

THERMAL STORAGE AND TRANSPORT R&D

SERI performs and subcontracts research on advanced thermal energy storage technologies. As shown in Fig. 1, research on direct-contact heat transfer between the thermal storage media and an immiscible heat transfer fluid is an important element in the SERI program because of the potential to reduce heat transfer costs appreciably. SERI is investigating thermochemical reactions as a low cost means of thermal energy storage and transport. Subcontractors are being supported to research innovative thermal energy storage and transport ideas. In all cases, the research will provide new information on these technologies which will allow assessment of their potential by developers.

SERI continued research on direct-contact heat transfer for thermal energy storage because the cost and performance penalties of conventional heat exchangers render many otherwise promising thermal storage concepts noncompetitive. Direct-contact heat transfer is particularly attractive for latent heat storage media or phase change materials (PCMs). PCMs have long been regarded as attractive for thermal energy storage because the storage volume required is much less than that for sensible heat storage. However, extensive heat-transfer area must be provided to overcome the thermal resistance of the storage medium during the energy extraction (freezing) cycle, and the cost of the heat exchange system must be reduced significantly for it to be competitive with conventional technology. Furthermore, the latent heat storage system must be capable of working with a heat transfer liquid since over 90% of the low- and medium-temperature solar thermal systems rely on liquid-based collectors. Finally, the volume for passage of the heat transfer liquid must be kept to a minimum to preserve the volume reduction of latent heat storage.

One possible means of meeting these requirements is to use bulk containment of the latent heat storage medium and direct-contact heat exchange between the storage medium and an immiscible heat transfer fluid to add heat to and remove heat from storage. In one such system, a tank holds the storage medium (Fig. 2). To add energy, hot oil is bubbled through the tank, melting the storage material. After rising through the PCM, the drops coalesce into a floating layer of oil. The oil is then pumped to the heat source and recycled through storage. To discharge the unit, drops of cold oil enter the bottom of the tank and absorb heat as they rise. After coalescing at the top, the warm oil is pumped to the load to deliver heat. As heat is extracted, flakes of solid PCM form, grow, and settle to the bottom of the tank.

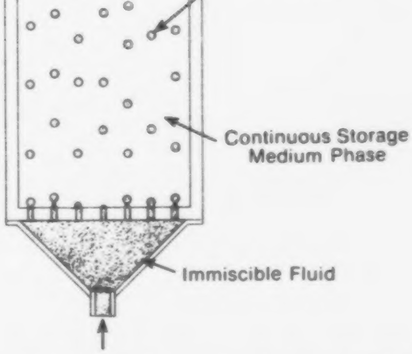

Figure 2. Direct-Contact Thermal Storage System for Heat Transfer Between a Latent Heat Storage Medium and an Immiscible Fluid

BEST DOCUMENT AVAILABLE

Despite the intriguing potential of direct-contact thermal storage, substantial uncertainties hinder the development and commercialization of the technology. Questions exist in the ability to reliably inject heat transfer oils into a freezing latent heat storage material. Also, the storage media may be carried out of the tank by the heat transfer oil and may freeze on external heat exchangers, thereby plugging the system. Finally, criteria are not available for designing a reliable heat exchange system.

The objective of the SERI direct-contact thermal storage research is to develop methods to ensure reliable distribution of the heat transfer fluid and to prevent carryover of the storage media. If these operational problems can be effectively overcome, design criteria will be determined for direct-contact thermal storage. As a result of this work, sufficient knowledge will be provided to the private sector to allow development of latent heat storage systems that cost less than existing systems and require about one-third the volume. In FY 1981, SERI is emphasizing research for low temperature storage because the technology has immediate application potential for home heating and domestic hot water uses and the experimental difficulties are less. However, the techology is applicable to high temperature applications as well; SERI will shift the research emphasis to high temperature direct-contact systems in FY 1982.

In FY 1981, SERI tested several different distributors in the low temperature, direct-contact storage experiment. A variety of difficulties were encountered in the operation of the distributors, but a distributor was found that reliably injected oil into a salt hydrate. After running through several freeze-thaw cycles with the design, the storage column was allowed to freeze overnight; no evidence of distributor flow blockage was observed when the system was started the next morning. A procedure was also developed to accurately measure continuous phase carryover, and experiments are now in progress to determine the extent of the carryover problem, factors affecting carryover, and methods to minimize the problem. Data are also being gathered to characterize the thermal performance of the unit.

In relation to the direct-contact research, the SERI Systems Analysis Task has identified the direct-contact latent heat storage concept being developed by Grumman Aerospace Corp. for high temperature applications as one of the three most promising storage concepts for water/steam central receivers. In the Grumman system, heat is extracted from a molten inorganic salt by bubbling drops of the salt through a cooler column of molten metal. As the salt rises, it solidifies into solid spheres, overflows at the top, and falls into the storage bin. Research into the operational characteristics of the unit is being carried out by Grumman under subcontract to SERI. Areas requiring further study include heat transfer and fluid flow phenomena within the heat exchanger, and heat transfer and freeze-up during droplet formation.

In another area, SERI has continued research on thermochemical energy storage and transport (TEST). This method of storage and transport involves absorption of energy by a reversible endothermic chemical reaction, with subsequent cooling to allow transport and/or storage at near-ambient temperatures. Upon demand, the energy stored in the chemicals is recovered by carrying out the reverse exothermic chemical reaction, with regeneration and recycling of the original chemicals.

Potentially, TEST systems can provide low cost, long-term thermal energy storage and long-distance thermal energy transport. However, previous studies have raised questions about the efficiency and costs of TEST (see reference 2). The major goal of the SERI task is to define TEST sufficiently to allow assessment of its long-term potential and identification of important research issues. The TEST definition involves thorough examination of both technical and economic aspects, as well as comparison with studies reported in the literature. Primary TEST systems are being designed, and cost consultants experienced in the costing of commercial reactor systems are estimating the price of the systems. Several independent groups are involved in this effort to provide a careful check of the results. The results will be integrated with applications to determine the delivered energy costs for the overall systems. Research will then be performed to clarify key assumptions in the analysis if promise is shown for TEST, and the analysis will be upgraded, if appropriate. The definition of TEST must be in sufficient detail so that if the outcome is favorable, the economic incentives will be obvious for private industrial firms and/or utilities to continue TEST R&D and commercialize the technology.

Currently, thermal energy storage concepts are being developed for several high temperature solar thermal applications. These so-called second-generation technologies offer cost and/or performance advantages over existing first-generation thermal energy storage options for six selected key applications. As part of the joint program plan between the DOE Division of Energy Storage Technology and the Division of Solar Thermal Energy Systems, SERI is subcontracting research on advanced storage technologies to significantly improve the cost and/or performance of thermal energy storage for high temperature solar thermal applications. Subcontractors were chosen competitively for this research. Research and analyses are being undertaken to determine the cost and performance potential of innovative thermal energy storage concepts so that judgment can be made as to whether these concepts can be effectively developed further. Since revolutionary approaches must be explored to significantly lower the cost of thermal energy storage, substantial risk is involved in this effort. The advanced storage technologies to be explored through this joint plan provide a basis for future focused thermal storage development efforts.

As one of the subcontractors in this effort, the University of Washington is investigating the phase conversion of small beads of a refracting oxide to a liquid in a solar furnace; silica, which is very stable at high temperatures, is an example of such an oxide. The liquid is stored until energy is needed; at this time, the molten material is injected into a heat exchanger under pressure as small-diameter streams, which break up into drops. The drops fall through a counterflowing, high pressure working gas, giving up their heat and solidifying into beads again.

In another innovative thermal storage study, the Institute of Gas Technology is studying a heat exchanger concept in which a composite sensible/latent heat storage media is maintained in direct contact with the high temperature air working fluid. A molten carbonate, phase change material is immobilized in porous refractories or particulate ceramic structures by capillary action, thus yielding a composite storage media.

As shown in Fig. 1, SERI is directing research on the transport of thermal energy. Thermal energy transport is important for supplying process heat from large central solar, coal, or nuclear plants to distributed users. Thermal transport is also essential for transmitting heat from distributed solar collectors to the centralized applications. For distances up to at least 50 km, thermal transport as sensible heat appears economically attractive, and this technology could service a significant market. Thermal transport by phase change materials may also have promise. For greater distances, advanced technologies such as thermochemical pipelines are more attractive.

In the thermal energy transport research area, SERI is initiating a subcontract to study the technical and economic merits of internal insulation of high temperature (120°-560° C) steam and hot water pipes. There is a strong economic incentive to develop cost-beneficial internal insulation in long-distance thermal energy transport systems. High temperature steam pipelines currently require expensive alloy steels and many expansion bends because of their high wall temperatures. For buried hot water systems, reinforced plastic pipes are economically advantageous in several important respects, but their present range of applications is severely temperature limited. Both sets of problems could be resolved by insulating the pipe walls from the high fluid temperatures.

The internal insulation study is the first phase of a wide-ranging SERI program planned in thermal energy transport research. Under SERI direction, the most economical thermal transport concepts will be optimized to refine the analysis and design system components. Research will be carried out to identify and develop the most cost-effective materials for transport, containment, and insulation. This activity will include definition of techniques to measure and retard system degradation. Alternate piping and insulation approaches will be explored, and materials and fluids will be evaluated to identify the most cost-effective options. Code qualification will be undertaken of the least costly containment materials capable of providing safe service in transport systems. In addition, efforts will be made to modify the codes to allow use of the least expensive, safe materials. Research and development will be performed on heat exchange concepts to reduce heat transfer costs. Advanced concepts identified in the cost analysis will be pursued. All of these activities will be performed in both the low and high temperature ranges with the objective of providing low cost thermal energy transport. The outcome of these activities will be a thermal transport technology base that can be used by industry and business to develop systems that will allow replacement of expensive oil and gas by low cost energy options.

SYSTEMS ANALYSIS AND ASSESSMENTS

A wide range of thermal energy storage and transport technologies have been researched. Systems analyses allow the technologies to be judged on a consistent basis for important applications. As a result, important technical and cost uncertainties can be identified for further research. In addition, nonpromising thermal energy storage and transport systems can be eliminated from the research program and the focus shifted to the most promising options.

SERI is continuing to perform systems analyses of thermal energy storage to support decision points in the Thermal Energy Storage for Solar Thermal Applications Program (TESSTA). In the TESSTA program, second- and third-generation thermal storage technologies will be developed to provide lower cost and/or improved performance over the first-generation technologies currently being deployed in solar thermal large-scale experiments (LSE). SERI is conducting the systems analysis of thermal storage to provide the information necessary to select thermal storage technologies for research development for specific solar thermal applications. The criteria to be met in this process are the following:

- The program cost goals defined in the plan must be met or surpassed.
- The advanced concepts must be more cost-effective than thermal storage technologies currently under development.

The program cost goals of the first criterion are based on the costs of the alternative energy systems, which establish the value of a solar thermal technology competing in the open market (see reference 3). Meeting these value-based goals ensures that there will be a market for the developed technologies. The second criterion requires comparison of the various thermal storage concepts (see reference 4).

During FY 1981, Stearns-Roger, under subcontract to SERI, completed cost and performance estimates of thermal energy storage for water/steam, organic fluid, and gas-cooled solar thermal receivers. Prior to completion of the work, Stearns-Roger presented the data to the developers of thermal energy storage technologies; 26 people representing 14 organizations attended the review. The data were generally well received, and only some fine tuning of the data was required to resolve the issues raised. The data was in good agreement with some independent assessments conducted by Combustion Engineering and Babcock and Wilcox under subcontract to Sandia National Laboratory, Livermore.

SERI integrated Stearns-Roger results with the solar thermal application to determine the impact of thermal energy storage on delivered energy cost. SERI also examined the sensitivity of the results to the following factors in the Stearns-Roger data: storage efficiency, cost of money, size and distribution of indirect cost factors, operation and maintenance cost assumptions, and cost uncertainties. The cost data had the largest effect, but the conclusions were unaffected within the range of uncertainties. The data were also compared with the cost goals for thermal energy storage. Based on the results, recommendations were made to the DOE Division of Energy Storage Technology on promising thermal energy storage concepts for continued study.

SERI also performs systems analyses of innovative thermal energy storage and transport concepts for solar thermal applications. The studies describe a system, estimate its cost, and compare the cost to the value. In this way, SERI identifies promising new concepts for existing and potential solar thermal applications. In FY 1981, mechanical transport of high temperature thermal energy was examined for ground-mounted thermal storage for solar thermal dish collector applications. Storage was evaluated for solar-powered air conditioning using trough collectors. These activities are reported in more detail in other papers presented at this meeting.

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PROJECT SUMMARY

PROJECT TITLE: Cost and Performance of Thermal Storage Concepts in Solar Thermal Systems

PRINCIPAL INVESTIGATOR: A. W. McKenzie

ORGANIZATION:
Stearns-Roger Services Inc.
P.O. Box 5888
Denver, Colorado 80217

PROJECT GOALS:

- To provide consistently calculated cost data for several thermal storage concepts in several solar thermal systems.
- To provide consistent and realistic performance data for thermal storage concepts integrated into solar thermal systems.
- To provide the above data as projected for a mature technology based upon the state-of-the-art and anticipated improvements in storage technologies.

PROJECT STATUS: The following has been accomplished in the course of this study:

- Available thermal concepts have been reviewed through a literature search, and contacts with the Solar Energy Research Institute, national laboratories, and other contractors.
- Reference systems were established in which the storage systems were compared.
- The systems selected for further study were established on the basis of a developed set of screening criteria.
- Schematics were developed for the remaining forty systems.
- Quantities were established for the above and rough-order-of-magnitude (ROM) costs computed.
- Based on the ROM costs and the screening criteria, candidates for further study were selected.
- Schematics will be more fully developed and costing was further refined for these twenty remaining systems.
- The results of the technical review were incorporated into the systems. Their storage range was expanded, and further costing refinements applied.
- The results of the thermal storage analysis were documented in a final report.
- Phase 2 of the study is currently in progress. This phase includes the conceptual design and costing of alternate thermal storage systems for liquid metal-cooled receivers.

Subcontract Number: XP-0-9001-1

Contract Period: March 1980 - March 1982

Funding Source: Solar Energy Research Institute.

C-23681

COST AND PERFORMANCE OF THERMAL STORAGE CONCEPTS IN SOLAR THERMAL SYSTEMS

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DENVER, COLORADO

ABSTRACT

The objectives of this study are as follows: to provide consistently calculated cost data, to develop realistic performance data, and to project that data for a mature technology for several thermal storage concepts integrated into several solar thermal systems. Available thermal storage concepts were reviewed through a literature search, and contacts with the Solar Energy Research Institute, National Laboratories, and other contractors. A screening criteria was developed which when applied, resulted in forty systems being judged suitable for further study. Schematics were made for these systems, quantities were established, and from these rough-order-of-magnitude costs were determined. Based upon those costs, candidate systems were further reduced. The remaining twenty systems were then more fully developed. A technical review was held in September, 1980; and the results of that review incorporated in the study. The storage ranges were expanded with further costing refinements being applied. The results of the thermal storage analysis was documented in a draft final report in April, 1981. A similar study for thermal storage for liquid metal receivers is now in progress.

INTRODUCTION

The Department of Energy has recognized the need for thermal storage systems adequate for commercial applications of thermal power systems and has prepared a plan to develop appropriate thermal technology. The Solar Energy Research Institute is supporting the implementation of that plan with a systems analysis of storage coupled solar thermal systems. Stearns-Roger is a subcontractor to SERI with the mission of providing cost and performance data for thermal storage concepts in solar thermal systems. The study carried out to meet that objective consists essentially of the following: establishment of reference systems, review of storage system concepts, development of criteria for assessing the systems, conceptual design, and costing of the systems.

STUDY OBJECTIVES

The primary objectives of this study are as follows:

- To provide consistently calculated cost data for several thermal storage concepts in several solar thermal systems.
- To provide consistent and realistic performance data for thermal storage concepts integrated into solar thermal systems.
- To provide the above data as projected for a mature technology based upon the state-of-the-art and anticipated improvements in storage technologies.

SCOPE

The scope of this study is limited to the evaluation of thermal storage concepts in the following solar thermal system applications:

- 100 MWe advanced water/steam central receiver solar electric power system.
- Organic fluid receiver for a 400 kWe total energy system, Shenandoah technology.
- 150 MWe closed Brayton cycle solar electric power system.
- Process heat applications using the water/steam and organic fluid receivers specified above, less the power conversion and related equipment.

SCREENING

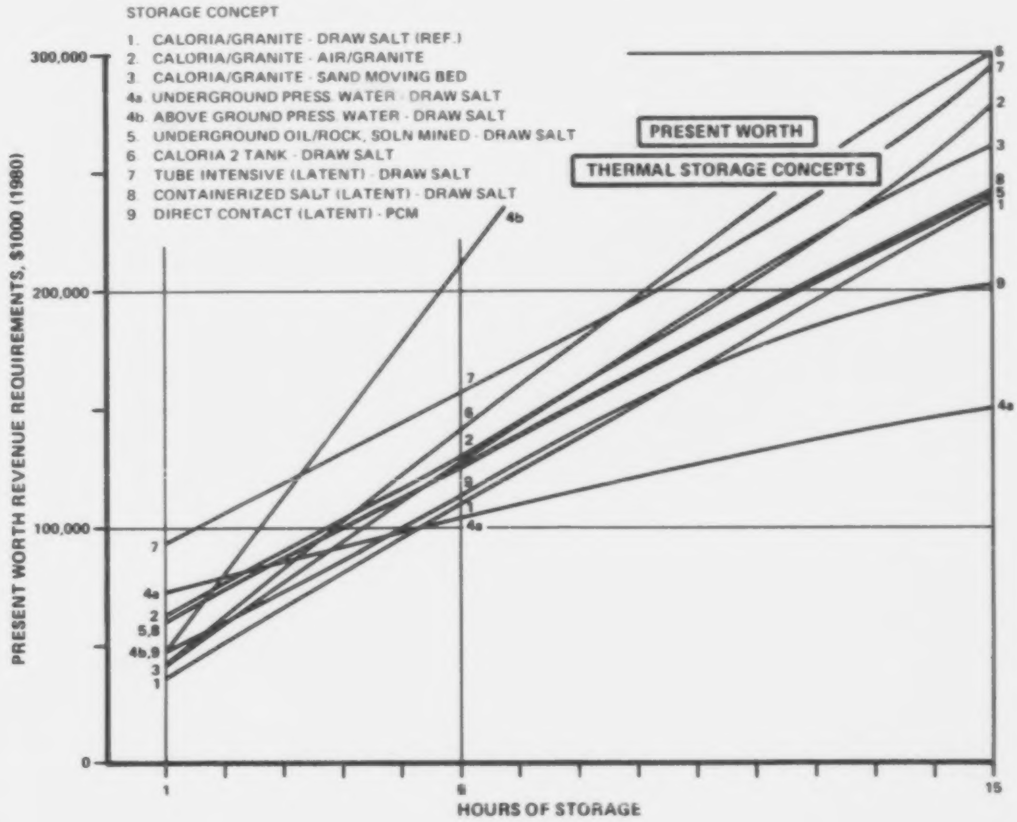
A concept screening task included a literature review of available data on thermal storage concepts; preliminary screening of potential storage concepts, reducing the total number of concepts to 40; and a final screening review wherein 20 storage concepts were recommended for conceptual design and costing for 1, 6 and 15 hours of storage.

Thermal storage concepts were compared using a present worth of revenue requirements (PWRR)economic method and reflect energy related equipment (tanks, insulation, etc.), power related equipment (pumps, compressors, fans, heat exchangers, etc.), storage media, installation and indirect costs, and first year variable costs, such as O&M, electrical energy and chemical usage.

STUDY RESULTS

Water/Steam Receiver (Power)

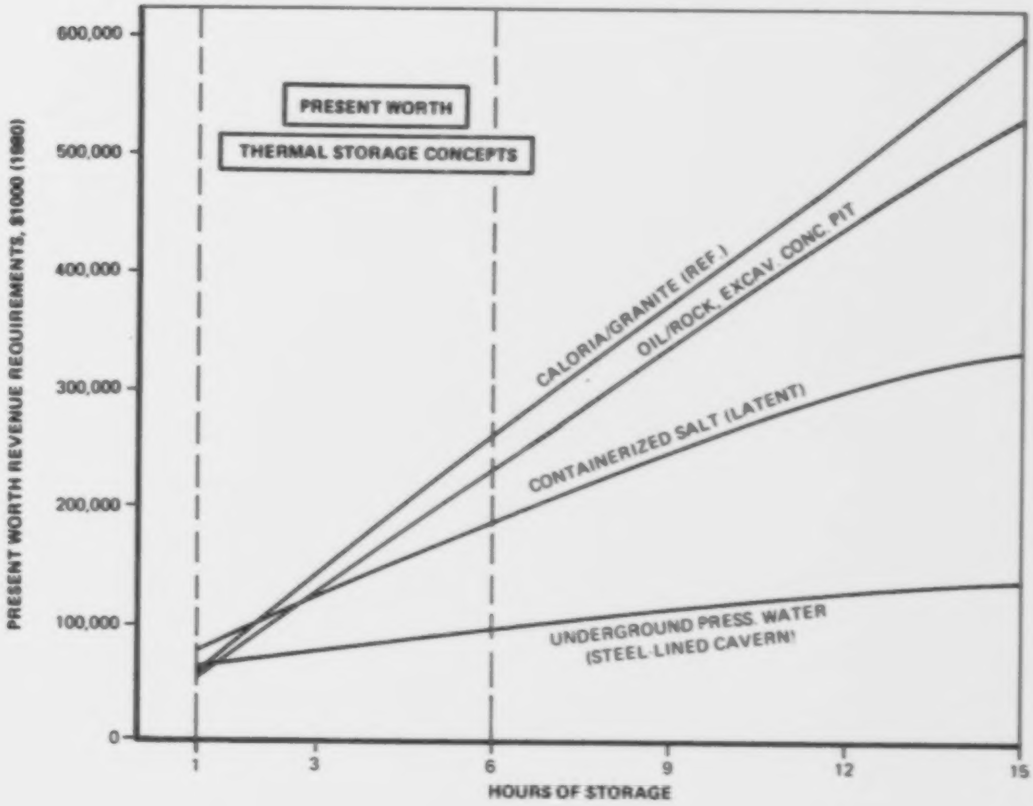
The PWRR vs. hours of storage for the water/steam receiver (power) application with the storage concepts studied is shown below. As indicated, the reference Caloria/granite-draw salt 2-stage storage concept is most economical below approximately 6 hours storage. Above 6 hours, underground pressurized water (steel-lined cavern) is the best 1st stage choice. Of the latent heat storage systems, the direct contact heat exchange system with a sensible heat 2nd stage using the phase change media appears attractive. A modified tube intensive heat exchange concept (not shown), utilizing an enhanced heat exchange surface, also appears very cost effective.



PRESENT WORTH REVENUE REQUIREMENTS, WATER/STEAM RECEIVER (POWER)

Water/Steam Receiver (Process Heat)

For the water/steam receiver process heat cases, supplying 288°C (550°F) saturated steam, the cost summary is shown below. For this specific application, underground pressurized water in a steel-lined cavern is the most economic by a wide margin.

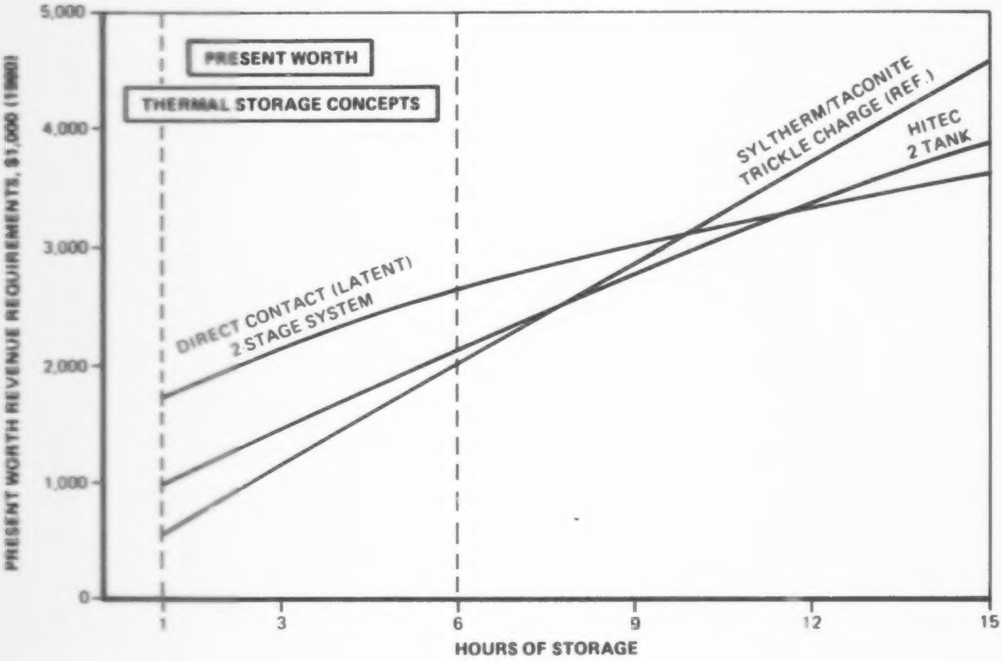


PRESENT WORTH REVENUE REQUIREMENTS,
WATER/STEAM RECEIVER (PROCESS HEAT)

Organic Fluid Receiver

The PWRR for the organic fluid receiver (power) thermal storage concepts are shown below. Below approximately 7 hours, the reference Syltherm/taconite, trickle charge, storage concept is the best choice. Below about 7 hours the Hitec salt (sensible) and direct contact (latent) systems become cost effective, owing primarily to high Syltherm 800 fluid cost and degradation.

For the organic fluid receiver process heat application nothing was identified with more promise than Caloria/granite or Caloria only (2 tank).



PRESENT WORTH REVENUE REQUIREMENTS,
ORGANIC FLUID RECEIVER (POWER)

Closed Air Brayton Receiver (Power)

The PWRR for the thermal storage concepts for the closed air Brayton cycle operating at 816°C (1,500°F) is shown below. Nothing was identified with significantly more promise than the reference air/alumina brick sensible heat storage system. A tube intensive latent heat system (not shown) was investigated and reported however its performance would be relatively poor.

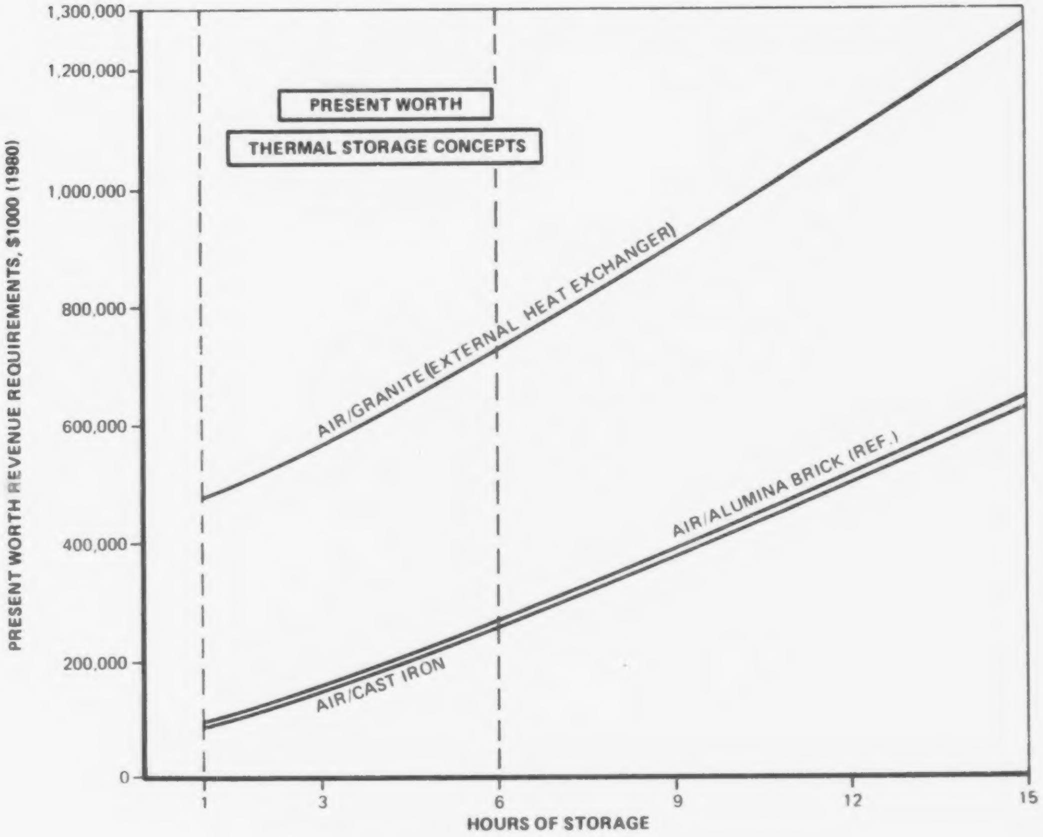


Figure 4–10. PRESENT WORTH REVENUE REQUIREMENTS, CLOSED AIR BRAYTON RECEIVER (POWER)

LIQUID METAL RECEIVERS

Phase 2 of this study includes the conceptual design and costing of alternate thermal storage systems for liquid metal-cooled receivers. The reference design selected was Rockwell International's 100 MWe Advanced Central Receiver Poweer System Sodium-Cooled Receiver Concept.

THERMAL STORAGE CONCEPTS

The thermal storage concepts being studies for liquid metal-cooled receiver include the following:

1. Liquid Metal, 2-Tank (Reference)
2. Molten Draw Salt, 2-Tank
3. Moving Sand Bed
4. Air/Rock
5. Tube Intensive Phase Change (C.E. Version)
6. Active Heat Exchange, Phase Change (Grumman Version)

For each thermal storage concept selected following the conceptual design review, Stearns-Roger will prepare detailed cost data for 1, 6 and 15 hours of storage. A final report will be prepared documenting all aspects of the Thermal Storage for Liquid Metal Receiver Study.

PROJECT SUMMARY

PROJECT TITLE: Systems Analysis of Thermal Storage

PRINCIPAL INVESTIGATOR: R. J. Copeland

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PROJECT GOALS: The objective of this project is to identify promising thermal storage concepts for research and development. The value of thermal storage concepts in solar thermal applications is analyzed to establish cost goals. Thermal Storage concepts are compared to each other using a consistent costing approach and accounting for the performance differences between the concepts. The best concept for specific applications are recommended for continued development. Analyses of new concepts and applications are also conducted to identify promising areas for research.

PROJECT STATUS: During FY 1981, analyses were conducted on thermal storage concepts for solar thermal applications. These studies include both estimates of the obtainable costs of thermal storage concepts and their worth to a user (i.e., value). Based on obtainable costs and performance, an in-depth study evaluated thermal storage concepts for water/steam, organic fluid and gas/Brayton solar thermal receivers. Promising and nonpromising concepts were identified. A study to evaluate thermal storage concepts for a liquid metal receiver was initiated. Value of thermal storage in a solar thermal industrial process heat application was analyzed. Several advanced concepts are being studied including ground-mounted thermal storage for parabolic dishes with Stirling engines.

CONTRACT NUMBER:	EG-77-C-01-4042
CONTRACT PERIOD:	October 1980 - September 1981
FUNDING LEVEL:	$388,000
FUNDING SOURCE:	Department of Energy, Office of Advance Conservation Technologies

SYSTEMS ANALYSIS OF THERMAL STORAGE

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ABSTRACT

During FY 1981, analyses were conducted on thermal storage concepts for solar thermal applications. These studies include estimates of both the obtainable costs of thermal storage concepts and their worth to a user (i.e., value). Based on obtainable costs and performance, an in-depth study evaluated thermal storage concepts for water/steam, organic fluid, and gas/Brayton solar thermal receivers. Promising and nonpromising concepts were identified. A study to evaluate thermal storage concepts for a liquid metal receiver was initiated. The value of thermal storage in a solar thermal industrial process heat application was analyzed. Several advanced concepts are being studied, including ground-mounted thermal storage for parabolic dishes with Stirling engines.

INTRODUCTION

The systems analysis of thermal storage effort is being conducted to identify promising thermal storage concepts for development. The criteria to be met in this process are

- The attainable cost must be less than or equal to program cost goals.
- The concept must be more cost-effective than alternative thermal storage technologies.

The program cost goals are being established to assure a marketplace for each developed technology. The development of cost goals requires an understanding of the potential marketplaces: the potential size of each market, the locations, user economic criteria, and alternative energy systems. From this knowledge, the cost of the most attractive alternative energy system is employed as a measure of what the user is willing to pay for a new energy system—that is, its value. The value of thermal storage is that part of the system value which is due to storage or which can be allocated to storage. The program cost goals for thermal storage are established based on the value of thermal storage.

The second criterion requires a direct comparison of the various thermal storage concepts. This analysis must be conducted with a consistent cost data base and for a specified application. Furthermore, to assure a fair comparison each technology must perform the same mission. The storage concepts are not required to have the same efficiency, but there must be a way of accounting for differences. A ranking methodology for conducting the comparisons has been developed by SERI (see reference 1), and SERI is employing that methodology in the analysis of the thermal storage concepts.

In FY 1981, this effort has focused on thermal storage for solar thermal applications. The value of thermal storage in solar thermal process heat applications was analyzed. Cost trade-off analyses were conducted for water/steam receivers, organic fluid receivers, and gas/Brayton systems. The potential for ground-mounted thermal storage with a parabolic dish/Stirling system was assessed. Studies of thermal storage technologies for liquid metal receivers, solar thermal electric power plants, and three advanced technology studies were initiated. Each of these activities is discussed in the following paragraphs.

VALUE OF THERMAL STORAGE

The value of thermal storage was analyzed for a solar thermal industrial process heat (IPH) application (see reference 2). The value of storage in an IPH system results primarily from backup fuel savings. Increased use of capital equipment (solar heat exchanger) and elimination of capital equipment (fossil-fueled backup boiler) contribute only slightly to storage value. Since the largest source of value is the saving of fossil fuels, parameters that affect the cost of solar energy or the cost of the backup fuel also influence the value of thermal storage. Significant parameters include the amount of insolation, the cost of the solar system, and backup fuel costs. High storage value results from a significant difference between the cost of the solar energy and the fossil fuel backup (i.e., when the solar cost is significantly less than the fuel cost).

Table 1 is a summary of the storage values and a comparison to typical storage costs. Costs for many concepts are higher, indicating additional research and development are required to make storage economically viable; there are also concepts which have equalled or cost less than the value.

Table 1. SUMMARY OF STORAGE VALUE

Duration (in hours)	Storage Value[+]	Storage Costs*
3 - 15	$\$10\text{-}\$30/\text{kWh}_t$	$\$10\text{-}\$100\ \text{kWh}_t$
15 - 100	$\$2\text{-}\$10/\text{kWh}_t$	NE
100 - 1000	$\$2/\text{kWh}_t$	NE

*NE = Not estimated.

[+] Dollars per unit storage capacity. Since storage is frequently used, the delivered energy cost is much less than these figures.

ANALYSES OF OBTAINABLE COSTS

Thermal storage concepts are being developed for solar thermal applications; a plan has been prepared as a cooperative effort of the Solar Thermal Program and the Thermal Energy Storage Program (reference 3). SERI is supporting decision points in that program by conducting comparative rankings of thermal storage concepts for identified applications. The first of these decision points occured in 1981. Thermal storage concepts were evaluated for the following solar thermal systems:

Water/Steam Central Receiver System

- Electric power plant; diurnal storage with a second-generation receiver.
- Process heat; diurnal storage with dry saturated steam delivered to the load.

Organic Fluid Receiver System

- Cogeneration system; weekend storage
  - Syltherm transfer fluid
  - Caloria transfer fluid
- Process heat; weekend storage with dry saturated steam delivered to the load.

Air-Cooled Receiver System

- Large Brayton cycle; diurnal storage.

Stearns-Roger, under subcontract to SERI, generated consistently calculated cost and performance data for thermal storage in these applications. SERI analyzed the impact of thermal storage on system-delivered energy cost (using the Stearns-Roger data) and evaluated the sensitivity of the study results. The Stearns-Roger work is described in another paper being given at this meeting and in S-R's final report (reference 4).

This study identified three thermal storage concepts with the potential to meet the program goals:

- Finned tube intensive latent heat
- Underground pressurized water
- Direct-contact latent heat

The concepts are listed in order of their priority for development.

THERMAL STORAGE FOR LIQUID METAL SOLAR THERMAL RECEIVERS

During FY 1981, a study was initiated to evaluate thermal storage for liquid metal solar thermal receivers. Stearns-Roger under subcontract to SERI is evaluating the cost and performance of several thermal storage concepts. On 6 August 1981, a review/workshop was held on this effort. Nine concepts were defined and costed for this review. Four concepts were selected for continued evaluation at 1, 6, and 15 hours of thermal storage capacity. The four are molten salt, air/rock, moving sand bed, and finned tube intensive latent. The remaining concepts (including liquid metal storage) had less potential and were eliminated from the study.

ADVANCED THERMAL STORAGE

Several advanced thermal storage subsystems are being evaluated for solar thermal applications. Two studies were completed on ground-mounted thermal storage for dish/Stirling systems. Thermal storage coupled combined cycles and direct-contact (air to draw salt) heat exchange were assessed.

Ground-Mounted Thermal Storage for Dish/Stirling Systems

Dish/Stirling systems have been shown to be one of the most promising solar thermal collector systems for small electric power systems (see reference 5). These systems employ buffer thermal storage mounted at each dish focal point, with a Stirling engine also mounted at the focal point. Diurnal storage is achieved through the use of batteries charged by the Stirling engine during the daytime. Studies were conducted to evaluate the potential for diurnal thermal storage as a replacement for the batteries. Because of the large masses required, the thermal storage must be mounted on the ground and some means of thermal energy transport is required. Two transport methods were evaluated: piping and mechanical.

Piping Transport

This model employs a cluster of dishes with centralized storage and Stirling engines. The number of dishes in a cluster was optimized; 19 was found to be the optimum number. Several transport media were considered; liquid sodium and liquid/vapor sodium (boiling in the receiver) were judged to be the best candidates. Two types of storage media and methods of charging and discharging storage were evaluated (tube intensive and direct-contact active heat exchanger). Two types of piping insulation, conventional and vacuum-jacketed multilayer (i.e., super insulation) were also evaluated.

Table 2 presents the results of the cost analysis of this study. The efficiency ratio is the ratio of electrical energy produced with the thermal storage to that produced with battery storage of the same capacity. Although the analysis was conducted with optimistic assumptions for the thermal storage (in performance, materials, and cost), cost figures were uniformly higher than those for battery storage. The study results were presented at the 16th IECEC (reference 6).

Table 2. Comparison of Thermal Storage to Battery Storage

Case	Efficiency Ratio	Breakeven Cost (1980$)	Cost (1980$)[a]	
			Nominal	Minimum
1. Liquid/vapor, vacuum jacket, tube intensive HX				
1a. $NaF-MgF_2$, 6 hr	0.99	12,500	18,700	16,500
1b. $NaF-MgF_2$, 3 hr	0.96	7,300	17,000	14,800
1c. $NaF-MgF_2$, 12 hr	1.03	13,500	21,000	18,800
1d. NaCl, 6 hr	0.98	11,500	20,100	17,900
2. Liquid/vapor, vacuum jacket, active HX				
2a. NaCl 6 hr	0.97	11,000	16,600	14,400
2b. NaCl 3 hr	0.94	6,500	16,400	14,200
2c. NaCl 12 hr	1.01	12,700	17,000	15,500
3. Liquid/vapor, conventional insulation, tube intensive, HX NaCl 6 hr	0.74	500	22,400	20,200
4. Liquid/liquid conventional insulation tube intensive, HX NaCl 6 hr	0.69	-1,500	23,100	20,900

[a] Cost per dish with 19-dish cluster, these costs include: storage media, tank, insulation, transport piping and insulation, receivers, pumps, factory fabrication of major components, and field installation. Direct costs only are presented.

Mechanical Transport

Due to the high costs found in the piping transport cases, SERI investigated an alternative method: mechanical transport of phase-change media. In this system, receivers are filled with phase-change media. The storage capacity is limited to one hour due to weight restrictions at the focus point. At hourly intervals, the entire receiver is removed mechanically (all phase media have been melted) and replaced with a new receiver (filled with solid media). The receivers are mechanically transported to a central area where the liquid media are drained and refilled with solid media. The liquid media are stored in a single large tank. Heat delivery is via direct contact (active heat exchange) to molten lead, solidifying the media into small pellets. The solid media are stored in a single large storage tank until needed to refill the receivers. The heated lead exchanges heat with the Stirling engine to generate electric power.

Figure 1 illustrates the layout of one version of the mechanical transport system. Portable loader-unloaders remove and reattach receivers to the parabolic dishes. These machines move around a loop (road) at a slow speed, making a complete round-trip in one hour. Faster moving mini-trains transport the receivers to the central section. Eight mini-trains, each carrying six receivers, make eight round trips per hour on each loop. (There are 350 dishes per loop and 2100 dishes in the field layout shown in Fig. 1.)

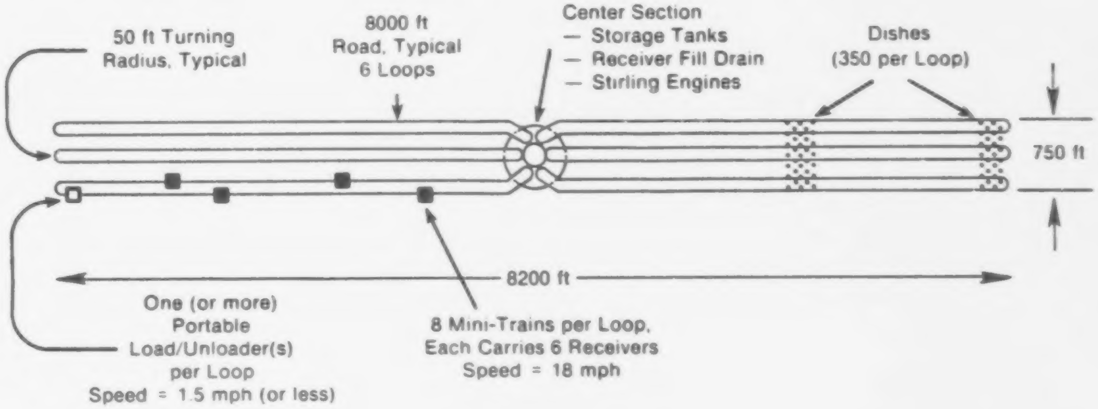
50 ft Turning Radius, Typical
8000 ft Road, Typical 6 Loops
Center Section
— Storage Tanks
— Receiver Fill Drain
— Stirling Engines
Dishes (350 per Loop)
750 ft
8200 ft
One (or more) Portable Load/Unloader(s) per Loop
Speed = 1.5 mph (or less)
8 Mini-Trains per Loop, Each Carries 6 Receivers
Speed = 18 mph

Fig. 1. Mechanical Transport Field Layout

Four types of mechanical transport were studied, and the relative ranking of each is shown below:

1. Mini-Train
   Six-receiver train car and separate transporter, two central storage tanks.
2. Large Truck
   Receivers filled and drained on each truck, with two central storage tanks.
3. Ski-Lift
   55 ft poles, one per dish; electric-drive cart rides on cables and carries one receiver with two central storage tanks.
4. Large Train
   Containerized salt and cars serve as both transporters and storage tanks.

The mini-train concept is shown in Fig. 1.

Very preliminary cost analyses were performed on each concept. The analyses indicated that there is a possibility that thermal storage costs would be less than those for battery storage. However, these costs were both optimistic and very preliminary. In addition, all mechanical transport concepts suffered from the following difficiencies:

• Interruptions in solar tracking	Loading and unloading receivers requires that the dishes not track the sun, resulting in lost collection time.
• Parasitic power	Not well defined, but significant amounts will be required to run the loader-unloaders, mini-trains, fill and drain, and active heat exchanger.
• Mechanical reliability	Several mechanical devices must operate in series for concepts to work, resulting, resulting in lost collected solar energy and large O&M costs.
• Competition with central solar thermal collection systems	System is an inherently large power system and thus must compete with molten salt central receiver and storage.

In large solar thermal systems (10 MW_e or larger), molten salt central receivers with storage have costs approximately equal to the dish/Stirling system (actually lower at high-storage capacities).* If the mechanical transport and storage system were successfully developed, then the anticipated result would be a system with costs approximately equal to the central receiver system. The development costs for the mechanical transport system would be very large. Due to the anticipated technical problems, high development cost, and low payoff, the study was terminated and additional research and development are not recommended.

Storage Coupled Air Brayton System

Solar central receiver systems are capable of producing temperatures on the same order as those used in gas turbines. A system capable of taking advantage of the low cost of gas turbine equipment, while retaining the benefits of molten salt storage and diurnal Rankine cycle operation, is the combined cycle. The combined-cycle plant has a high thermal efficiency (45.4%) and a unit capital cost competitive with a molten draw salt-steam Rankine solar thermal plant. In the combined-cycle plant, inlet ambient air is compressed, preheated by the exhaust air, then heated to 815°C (1500°F) in the receiver. After passing through the turbine, exhaust air at 600°C (1110°F) is passed through a direct-contact heat exchanger where it cools from 600°C to 300°C and raises the temperature of counter flowing drops of molten draw salt from 288°C to 565°C. The salt is then circulated through a steam generator to provide the energy input for a Rankine cycle plant, or it is stored to run the generator at a later time. The economics of the direct-contact heat exchanger system was examined.

Figure 2 presents the busbar energy cost for the three cycles as a function of capacity factor, normalized to the cost of the base molten salt cycle at a capacity factor of 0.65. The direct-contact combined cycle shows an advantage at low capacity factors but not at high capacity factors. While the differences in cost are less than the uncertainties in the calculations, it must be remembered that the combined cycle is not optimized and has a large potential for improvement. It can also be seen that the use of gas turbines without storage gives the combined cycle an inherently low capacity factor, unless oil burners are used to extend its operation. However, use of oil is an option with this system, not a required feature.

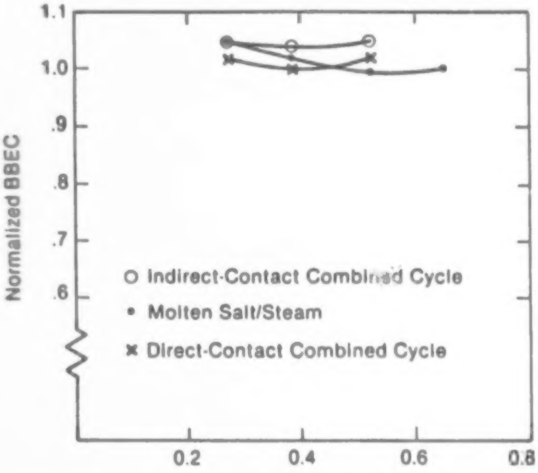

Fig. 2. Normalized Busbar Energy Cost vs. Capacity Factor for 1500 F Turbine Inlet on Combined Cycles

Possible improvements to the solar section include terminal concentrators and receiver and field size optimization. Use of a high-pressure closed Brayton cycle with helium as a working fluid would reduce heat exchanger costs and eliminate the need for salt treatment. Optimizing the size and effectiveness of the regenerator and receiver heat exchanger would also lower their cost. Raising the turbine inlet temperature would increase cycle efficiency; analyses indicated a system operating at 2000°F would be more efficient despite reduced receiver efficiency.

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*Cost of point-focus central receiver/Rankine is 94 mills/kWh_e versus dish/Stirling at 96 mills/kWh_e at 10 MW_e, 0.7 capacity factor. See reference 5.

Lowering the temperature at which heat is rejected to the Rankine cycle would also improve net efficiency by allowing increased regeneration. Based on this data, the following conclusions seem reasonable:

- The combined-cycle system is competitive with molten salt. Potential improvements identified may make the concept even more attractive.
- Direct-contact heat exchange provides significant cost advantages over conventional compact heat exchangers.
- At solar capacity factors over 0.5, an all-molten salt cycle is preferred to a combined cycle.

A paper on this study was presented at AS/ISES in May 1981 (7).

WORK IN PROGRESS

Advanced thermal storage concepts are also being evaluated for solar thermal applications. These analyses are not complete as of this writing and are noted below:

A. Thermal Storage for an Absorption Air Conditioning Cycle

This concept employs a parabolic trough solar thermal collector. Heat is collected at approximate 200°C (400°F) and drives a two-stage lithium bromide absorption cycle.

B. Very High-Temperature Molten Salt Storage for a Central Receiver

Solar thermal applications include a) fuel and chemicals, b) process heat, and c) electric power. These users sometimes require heat up to 1100°C (2000°F). Currently, molten salt storage and receivers are indicated to be among the most attractive solar thermal central receivers (see reference 8) but are temperature limited to 566°C (1050°F). This study is investigating the use of carbonates, chlorides and sodium hydroxide for a molten salt receiver and storage for the high-temperature applications (e.g., thermochemically generated hydrogen).

FY 1982 PLANS

The current plans for the systems analysis task are to complete 1) the evaluation of thermal storage for liquid metal receivers, and 2) the advanced concept studies in progress. The very high-temperature molten salts currently appear promising and exploratory research is also planned.

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THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT

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1617 Cole Boulevard
Golden, Colorado

ABSTRACT

This paper describes SERI's research program in thermochemical energy storage and transport, with current emphasis on a study to define concept feasibility. A heat utility system is under study which uses either direct thermal transport and storage (draw salt) or any of five thermochemical transport and storage systems. Preliminary results indicate large investment requirements and low efficiency, resulting in a relatively high delivered-energy cost.

INTRODUCTION

Thermochemical energy storage and transport (TEST) involves absorption of high-quality thermal energy by an endothermic, reversible chemical reaction to convert an energy-poor material to an energy-rich one. This material is cooled and may be saved for later use or transported for use at a remote location away from the energy source. On demand, high-quality thermal energy is recovered by performing the reverse exothermic chemical reaction to regenerate the energy-poor material, which may be stored or transported back to the energy source to repeat the cycle. Reversible chemical reactions present the possibility of high-efficiency, long-duration storage or high-efficiency, long-distance transport of high-quality thermal energy.

Figure 1 shows a simple schematic of a TEST system; major elements are indicated as reactors, heat exchangers, storage vessels, and the method of transport. This schematic is deceptively simple because the process actually involves a potentially complicated and costly chemical processing plant at both the source and sink. The efficiency of either the storage or transport system is important, because inefficiencies are levered back into the cost and size of the heat source. Chemical process plants usually tend to be relatively high-investment plants that are typically justified by the high value of a specialized product. Two concerns, high investment and low efficiency, could result in unacceptably high delivered-energy cost.

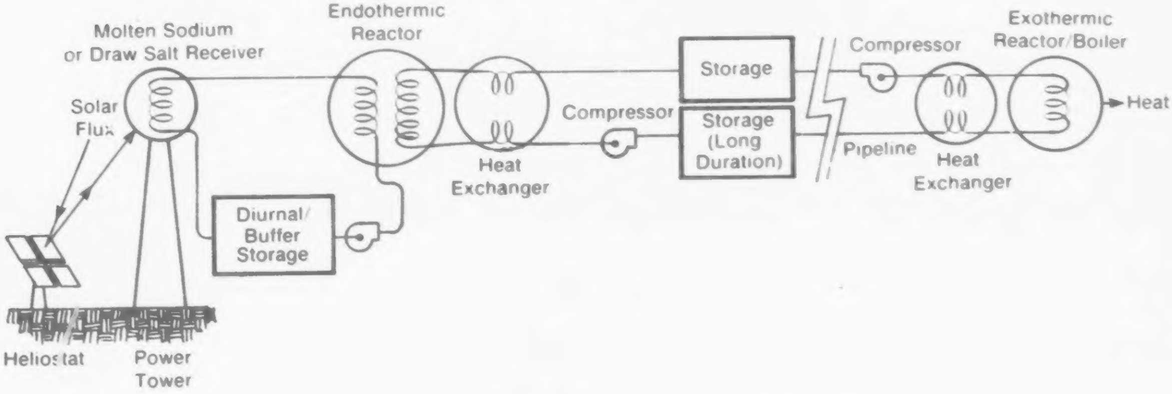

Figure 1. Thermochemical Energy Storage and Transport

The objectives of the SERI TEST program are to

- determine the technical feasibility of TEST,
- determine the economic feasibility of TEST,

- define areas of significant research opportunities, and
- define potential applications of TEST.

The result of this study will be recommendations about future TEST programs, funding levels, and applications.

BACKGROUND

Thermochemical energy storage and transport have been the subjects of several research programs in recent years. Methodical searches have been performed to identify the prime candidate reaction systems (see Refs. 1 and 2). Both JPL (Ref. 3) and Sandia National Laboratory Livermore (Ref. 4) have had TEST programs and have performed partial analyses. Both studies have come to the conclusion that efficiencies may be too low to justify additional research for storage applications of TEST. These studies were well done; the SERI TEST program has built on the prior work. The consensus seems to be that, even though the previous studies may have arrived at the proper conclusion with respect to thermochemical energy storage, a thorough definition of the delivered energy cost on which to base a final judgment is required. Past studies are not definitive for thermochemical energy transport applications.

PROGRAM STRUCTURE

The SERI thermochemical energy storage and transport program has two major elements: a feasibility analysis and an experimental program. Equipment has been assembled in the experimental program that is both capable of answering technical uncertainties as they arise and suitable for additional research into both catalytic and noncatalytic reaction systems. This paper describes the feasibility study, which is the major program element.

The feasibility study is structured to give an engineering appraisal of the technical and economic merits of thermochemical reaction systems used for either energy transport or storage. The basic steps of the feasibility study are as follows:

- process definition, including flowsheets with heat and mass balances;
- equipment descriptions, including type, size, and material of construction;
- estimates of cost of equipment, total plant investment, and operating cost;
- determination of that portion of the cost of delivered energy accorded to storage and/or transport through use of an economic model;
- determination of the effect of study assumptions and estimation of uncertainties on the delivered energy cost;
- judgment of technical feasibility, based especially on the process flowsheet and equipment calculations.

For this study, a utility system is structured as shown in Fig. 2. The original intent was to examine heat delivery to the user for either production of heat or electricity. Thus, the system basis was to deliver 100 MW_e (38% generation efficiency) or 262 MW_t (895×10^6 Btu/hr). However, after discussions with the Electric Power Research Institute about efficiency of electricity transmission, transporting heat between two points for production of electricity at the final point seems unjustified. Generating electricity at the heat source and transporting electricity is more cost-effective because it is more efficient. Thus, the study system is structured as a heat utility; a single heat source supplies industrial process heat to 10 users in an industrial area 50 miles away, and each user is located one-half mile from the main transmission line. The length of the transmission line can be adjusted to any distance. Because most of the transport systems are gaseous, the transmission line is typically a pipeline; since the applications are closed loop, there is a parallel return line.

The system is such that a thermal energy storage subsystem can be inserted at any point in the line, and either direct thermal transport or thermochemical energy transport can be used. The system model is general enough that any heat source can be considered, although a central receiver solar collector system was used. The solar subsystem uses either molten sodium or molten draw salt as a working fluid and includes diurnal storage as part of the collector subsystem. The endothermic chemical reactor is coupled to the heat source through the working fluid. Direct radiative coupling was not considered. The end product is 600 psi/400° C (750° F) superheated steam for industrial process heat. No credit is assumed for rejected heat.

One goal of the feasibility study is to be as realistic as possible within the constraints of timing and funding. SERI has overall responsibility for study definition, execution, interpretation of results, and final recommendations. To broaden the perspective and to ensure realistic bases and methods, SERI has enlisted a team of three independent, industrial consultants and two academic consultants. The function of the industrial consultants is to review and revise the SERI flowsheets and equipment scopes, do the actual estimating, and make critical process appraisals. The two academic consultants will make an independent assessment of the study structure, methods, and results and will assist with the overall economic model. These relationships are shown in Fig. 3.

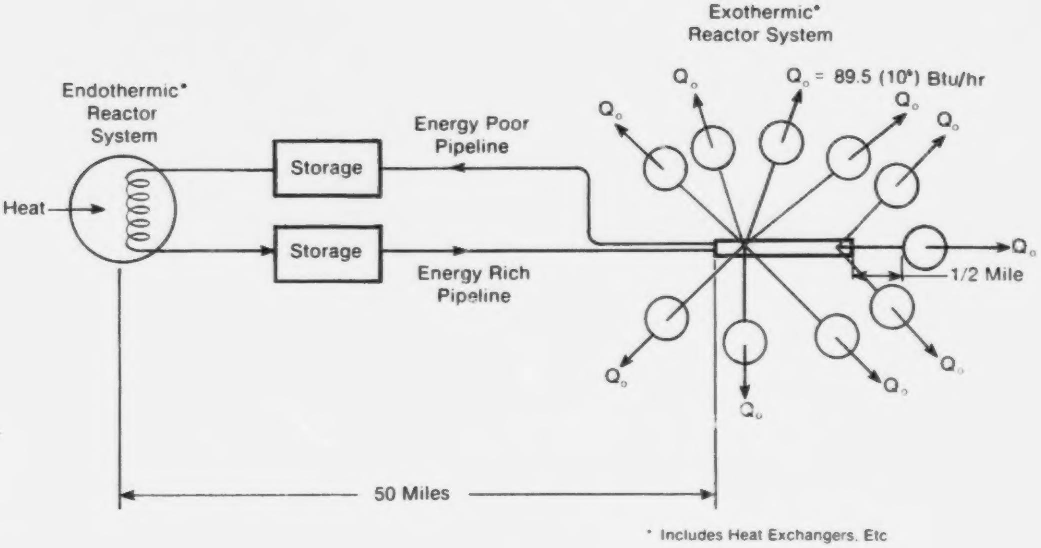
Exothermic*
Reactor System
Q$_o$ = 89.5 (10^6) Btu/hr
Q$_o$
Endothermic*
Reactor
System
Heat
Storage
Storage
Energy Poor
Pipeline
Energy Rich
Pipeline
1/2 Mile
50 Miles
* Includes Heat Exchangers, Etc

Figure 2. TEST Heat Utility Model

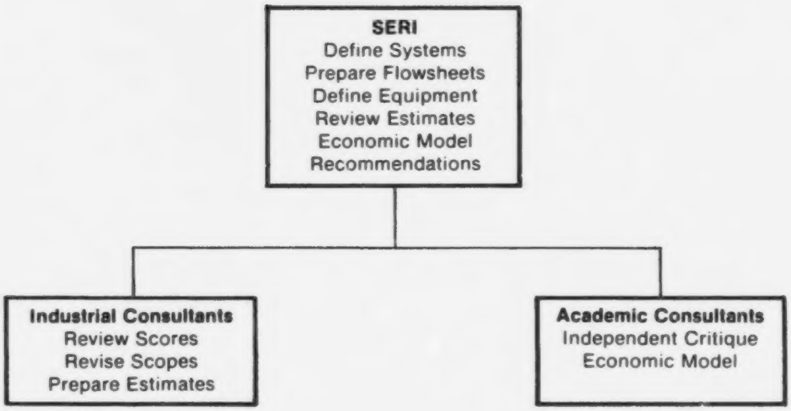
SERI
Define Systems
Prepare Flowsheets
Define Equipment
Review Estimates
Economic Model
Recommendations
Industrial Consultants
Review Scores
Revise Scopes
Prepare Estimates
Academic Consultants
Independent Critique
Economic Model

Figure 3. TEST Task Organization.

TRANSPORT AND STORAGE SYSTEMS

The following thermochemical systems were chosen for inclusion in this study:

- $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$
- $CH_4 + H_2O \rightleftharpoons CO + 3H_2$
- $2SO_3 \rightleftharpoons 2SO_2 + O_2$
- $Ca(OH)_2 \rightleftharpoons CaO + H_2O$
- $2NH_3 \rightleftharpoons N_2 + 3H_2$

A literature review has indicated that these systems are the most promising candidates. The delivery temperature potential varies; however, all systems have been defined in such a way that they deliver the same quality product [600 psi/400° C (750° F) steam]. This is not viewed as a significant disadvantage for any of the systems.

The primary alternatives against which TEST subsystems can be compared are direct thermal storage (draw salt tanks) and direct thermal transport (draw salt pipeline). The storage tanks were patterned after those of Martin Marietta (see Ref. 5). The alternatives against which this heat utility concept can be compared are direct fossil fuel use and electric resistance heating.

STUDY PROGRESS AND PRELIMINARY RESULTS

System flowsheets, equipment descriptions, and the bulk of the estimating are complete. Work on the system model is under way. Results to date indicate the following:

- Overall thermochemical energy storage and transport efficiencies are very sensitive to chemical process definition. Even with a well-defined process, efficiencies are low (less than 70%).
- Practical engineering constraints have a considerable effect on system efficiency. Theoretical flowsheets without practical constraints result in misleadingly high efficiencies. Poor engineering can result in low, even negative, efficiencies.
- Investment can be extremely high; e.g., (typical) ~$400M for the CO_2-CH_4 transport system and ~$750M for the CO_2-CH_4 transport system, with 100 hours of salt-cavern storage. Innovations will be required to obtain reasonable system investments.
- Investment for direct thermal transport and storage (100 hours) using molten draw salt is also extremely high and is greater than the CO_2-CH_4 thermochemical system. This indicates that innovative research will be required to transport energy (for end-use heat) by some means.

FUTURE WORK

In September 1981, SERI will issue preliminary results and make appropriate recommendations to DOE about future thermochemical energy storage and transport research. The preliminary results of this study, which has attempted to be realistic in process definition, appear to be negative. In FY 1982, SERI will review the work with all persons who have an interest in TEST systems and include other thermochemical concepts for storing or transporting thermal energy as appropriate. If the final results of this study are sufficiently negative that no additional research on thermochemical energy storage and transport appears justified, then it must be established that no significant systems or innovations have been overlooked and that assumptions used are valid. Future work will then bring this study to a timely conclusion, with resultant recommendations to DOE by the end of FY 1982.

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PROJECT SUMMARY

Project Title:	High Temperature Active Heat Exchanger Research for Latent Heat Storage
Principal Investigator:	J. Alario, R. Haslett
Organization:	Grumman Aerospace Corporation Bethpage, N.Y. 11714 Telephone: (516) 575-2433/3924
Project Objectives:	Develop an active method of heat exchange in a latent heat (salt) thermal storage system that prevents a low thermal conductivity solid salt layer from forming on heat exchanger surfaces.
Project Status:	Under an initial DOE/NASA-Lewis contract, a modular test unit of 10KW heat transfer rate and 10KW-Hr storage was designed and fabricated to investigate heat transfer by direct contact between molten salt and a liquid metal eutectic carrier fluid. The concept selection, evaluation and design phases of that program have been published in Topical Report No. NASA CR 159726 (January 1980). The test evaluation phase for the direct contact heat exchanger concept, as originally conceived, started mid-February 1980, but was interrupted in June due to funding limitations. Various problems with the pumps, plumbing leaks and corrosion failure of electrical heaters contributed to delays. At the time of interruption, the media transfer technique had been verified, liquid metal was circulated through the heat exchanger, all system components were preheated and the salt system was about to be activated. The program is now being resumed under DOE/SERI sponsorship to refurbish hardware and continue test evaluation. Contract negotiations are in progress.
Contract Number:	In negotiation
Contract Period:	12 months
Funding Level:	TBD
Funding Source:	Solar Energy Research Institute

HIGH TEMPERATURE ACTIVE HEAT EXCHANGER RESEARCH FOR LATENT HEAT STORAGE

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Grumman Aerospace Corp.
Bethpage, N.Y. 11714

ABSTRACT

The objective of this program is to develop an active heat exchange method in a latent heat (salt) thermal energy storage system that prevents a low conductivity solid salt layer from forming on heat transfer surfaces. An evaluation of suitable media with melting points in the temperature range of interest (250 to 400°C) limited the candidates to molten salts from the chloride, hydroxide and nitrate families, based on high storage capacity, good corrosion characteristics and availability in large quantities at reasonable cost. The specific salt recommended for laboratory tests was a choride eutectic (20.5KCL o 24.5NaCL o 55.0$MgCl_2$% by wt.), with a nominal melting point of 385°C.

Various active heat exchange concepts were given a technical and economic comparison to a passive tube-shell design for a reference application (300 MW_t for 6 hours). Test hardware was then built for the most promising concept: a direct contact heat exchanger in which molten salt droplets are injected into a cooler counter-flowing stream of liquid metal carrier fluid (Lead/Bismuth).

The initial test evaluation was interrupted due to funding limitations resulting from various problems with pumps, plumbing leaks and corrosion failure of electrical heaters. Earlier decisions to select some non-optimum components, which were based on budget limits, proved ill-advised. Plans have been submitted to SERI for completing the program after detailed inspection and hardware refurbishment.

INTRODUCTION

Thermal energy storage is a promising method for extending the steam generating capabilities of both conventional fossil fuel power plants and advanced solar thermal energy conversion systems. Excess thermal energy available from the steam boiler (or concentrating solar collector) can be stored during off-peak demand periods and then used to increase steam capacity during peak load periods. In a solar application, this stored energy would be substituted for the primary source during non-sunlight periods.

Thermal energy can be stored as the heat required to induce a temperature change, a phase transformation (e.g., solid to liquid), or a chemical change in a suitable medium. Using the latent heat of fusion (phase change) is attractive because the heat absorbed per pound of storage material is relatively high, resulting in a more compact system. Molten salts and salt eutectics are particularly attractive as phase change media because of their high weight and volumetric heat storage capabilities, their abundance in nature and as the result of industrial processes, and their low cost per unit storage capability.

Related studies have shown that a latent thermal energy storage system which utilizes a conventional passive tube and shell heat exchanger for salt containment is both technically and economically feasible. Suitable latent heat media are inexpensive, but a major portion of the cost is related to the passive heat exchange process. The accumulation of salt deposits on discharge tube surfaces, combined with a high thermal resistance of the solid Phase Change Material (PCM) requires a large (and costly) heat exchanger surface area. Thus, significant performance and cost benefits can be realized if an active heat exchange concept can be developed which prevents the buildup of a solid salt layer on the heat transfer surfaces.

The overall objective of this program is the continued development of an active heat exchanger for latent heat storage which is suitable for utility applications. These include either conventionally fueled plants or advanced solar central receiver power plants. An effective TES system would be used to supply peak energy requirements with energy stored during the off-peak periods. For conventional power plants this offsets the need to increase the plant boiler capacity, whereas advanced solar power plants require thermal energy storage for buffering during normal operation and as the primary energy source during non-sunlight hours.

DISCUSSION

TES Media Selection - At utility operating temperatures suitable phase change materials are confined to molten salts and salt eutectics. An evaluation of candidate materials considered the following criteria: melting point, latent heat of fusion, heat storage capacity (kWH_t/unit volume) corrosion characteristics, handling problems, availability and cost. Of the candidate salts considered, three families were found best suited for this TES application: chlorides, hydroxides and nitrates. The specific salts recommended, in order of preference, were as follows:

1. 20.5KCL o 24.5NaCl o 55.0$MgCl_2$, % by weight - A chloride salt eutectic that melts at 385°C (725°F)
2. KOH - Potassium hydroxide, melting point at 360°C (680°F)
3. $NaNO_3$ - Sodium nitrate, melting point at 307° (585°F)

All three salts have good thermal performance, few corrosion problems - which permits the use of less expensive containment materials (e.g., mild steel), and they are available in large quantities at a reasonable cost. The chloride salt eutectic was selected for the demonstration test evaluation since it best fits the steam generating requirement (350°C) of advanced solar power plants.

Heat Exchange Concepts - Two active heat exchange concepts were originally selected for demonstration hardware development:

- Direct contact heat exchanger
- Rotating drum with fixed scraper

These were chosen from among the various concepts considered (scrapers, agitators, vibrators, slurries) because they exhibited the best combination of low development risk and high cost benefit. Unit cost estimates for the chosen TES concepts as applied to a 300 MW utility application with 6 hr of storage were 16 $\$/KWh_t$ compared to 21 $\$/KWh_t$ for a reference passive tube-shell design. Funding limitations restricted testing to only one concept and the direct contact heat exchanger was preferred as the simplest approach.

Development test modules were designed to interface with an intermediate heat transport loop which uses a liquid metal eutectic fluid (44.5Pb/55.5Bi% by wt.). Three separate tank modules are provided: 1) a liquid metal tank which serves as a supply reservoir and contains the pump, 2) a molten salt tank which contains the PCM supply and a pump, and 3) a central heat exchange module within which the heat transfer between the molten salt and liquid metal occurs. All materials were primarily 1020 mild steel, except the plumbing which was stainless steel. A nitrogen gas blanket was used to prevent atmospheric contamination.

Direct Contact Heat Exchanger - The direct contact heat exchange concept is illustrated in Figure 1. Three tank modules are coupled by two separate fluid loops; one for the molten salt, the other for the liquid metal carrier. The salt serves as the thermal energy storage medium, while the liquid metal transfers the stored energy to the eventual heat sink, in this case an air stream. Separate streams of salt and liquid metal, which emanate from their respective tanks, are mixed together in the heat exchange reservoir. Both latent and sensible heat are transferred to the cooler liquid metal by the countercurrent flow of molten salt bubbles which are injected at the bottom of the metal column. As the salt solidifies, it rises to the top of the heat exchange reservoir, where it is directed over the edges, falling to the bottom of the surrounding tank. It is held here until the next charging cycle, when it is melted (by electrical heaters which simulate the heat source) and drained into the molten salt tank. Another discharge cycle can then begin. Photographs of the test hardware are shown in Figures 2 (before insulation) and 3 (after insulation with JM Cerablanket).

Test Experience - Testing of the direct contact heat exchanger was interrupted due to a series of difficulties with the pumps, plumbing and electrical heaters. The hardware, expecially the heaters, needs refurbishment before testing can be resumed. Although definitive test results cannot be reported at this time, our experience might benefit others. A summary of the most significant observations follows:

- In general we found that the size of the test module resulted in slow and difficult repairs since it took days to heat up and cool down.

BEST DOCUMENT AVAILABLE

- Relatively inexpensive air-motor-driven submersible-type pumps were used for which seals had to be provided. Improper seal design resulted in bending of the pump shafts due to differential thermal expansion and necessitated rework to create a much looser than desired fit. Thus, we could not continuously pressurize the system with a nitrogen gas cover blanket, but instead used periodic gas purges. Using a more expensive presealed pump/motor assembly would have been cheaper in the long run.

- Early problems were encountered with swageloc fittings, some of which leaked at operating temperature. The problem was solved by tightening all connections while heating them with an acetylene torch.

- By far the most troublesome of the problems resulted from our decision to use less expensive manual heater controls. Human error during the initial system checkout resulted in over powered band heaters and numerous heater and instrumentation failures. In hindsight, every common heater circuit should have automatic controllers backed up by a direct reading of the sheath temperatures.

- The immersion heaters were very prone to failure. Over an effective period of about four weeks operating time, the following failures were experienced: Lead system (4 of 5 failed); Salt system (8 of 8); heat exchanger module (5 of 6). The exact cause of failure has not yet been determined, although it is most likely some combination of corrosion and hydraulic action from the many freeze/melt cycles. A careful post-test inspection is planned prior to refurbishment. These problems indicate that special consideration must be given to methods of heating and cooling that involve immersed tubes.

- After a period of about two weeks the threaded fittings for the immersion heaters on the salt module began to leak salt vapor. (These connections used tapered threads and a high temperature sealant). The escaping vapor, when combined with atmospheric moisture, prove particularly troublesome. All of the terminals on the band heaters in the vicinity of the leaks quickly corroded and caused heater failures, which necessitated several changes to band heaters during the testing. There also was evidence that leaks were coming through the main terminals of the immersion heaters which means that the sheath over the heating element had been broken inside the tank.

- The external salt tank surface in the vicinity of the immersion heaters was badly corroded due to the aforementioned salt leaks. Since the extent of any internal corrosion was unknown, ultrasonic tests to determine the net wall thickness were taken. The results indicated a decrease of 10 mils from the original 1/4 inch thickness, which confirmed that only the external surface was being corroded.

- Over-loading of line heaters occurred due to poor axial heat conduction between heater elements, which were too widely separated. To avoid this problem, trace heating should be applied to as much line as possible.

- The use of a thermocouple tree to thermally sense the level of liquid metal and molten salt proved very reliable. These were used as backup to commercial level sensors which were the primary means of level indication in the heat exchange reservoir.

- During the checkout testing it became necessary to change the utility cooling fluid from water to air. This was done to avoid freezing of liquid metal due to nucleate boiling in the water line resulting from excessively high temperature differences.

Future Effort

The following tasks are planned under the follow-on SERI program:

- Examine present test set-up
- Refurbish hardware as needed
- Complete testing
- Major changes to improve reliability

  - upgrade pumps
  - all welded couplings
  - eliminate immersion heaters
  - 100% trace heating of lines
  - automatic controllers for heaters

- Features added to correlate analysis
  - sample scoop for measurement of diameter and density of droplets
  - additional instrumentation

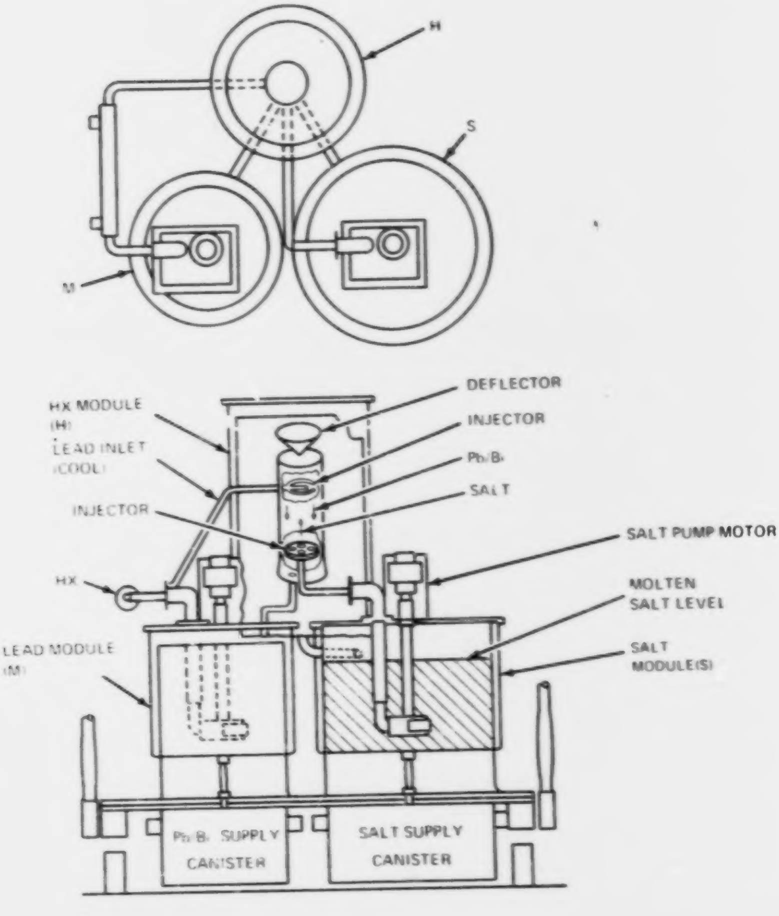
H
S
M
HX MODULE (H)
LEAD INLET (COOL)
DEFLECTOR
INJECTOR
Pb/Bi
SALT
INJECTOR
SALT PUMP MOTOR
HX
MOLTEN SALT LEVEL
LEAD MODULE (M)
SALT MODULE(S)
Pb/Bi SUPPLY CANISTER
SALT SUPPLY CANISTER

FIGURE 1 - DIRECT CONTACT HX CONCEPT

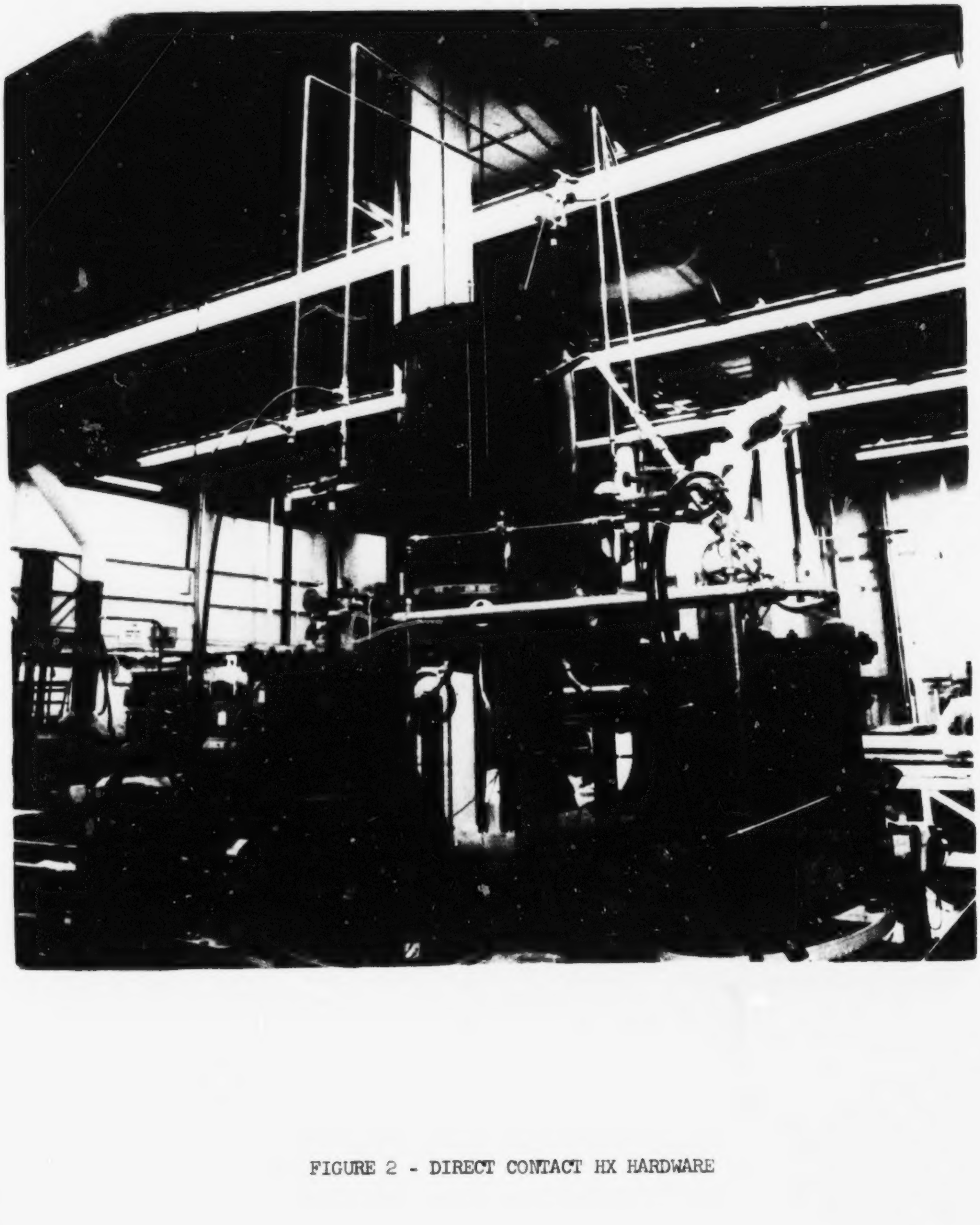

FIGURE 2 - DIRECT CONTACT HX HARDWARE

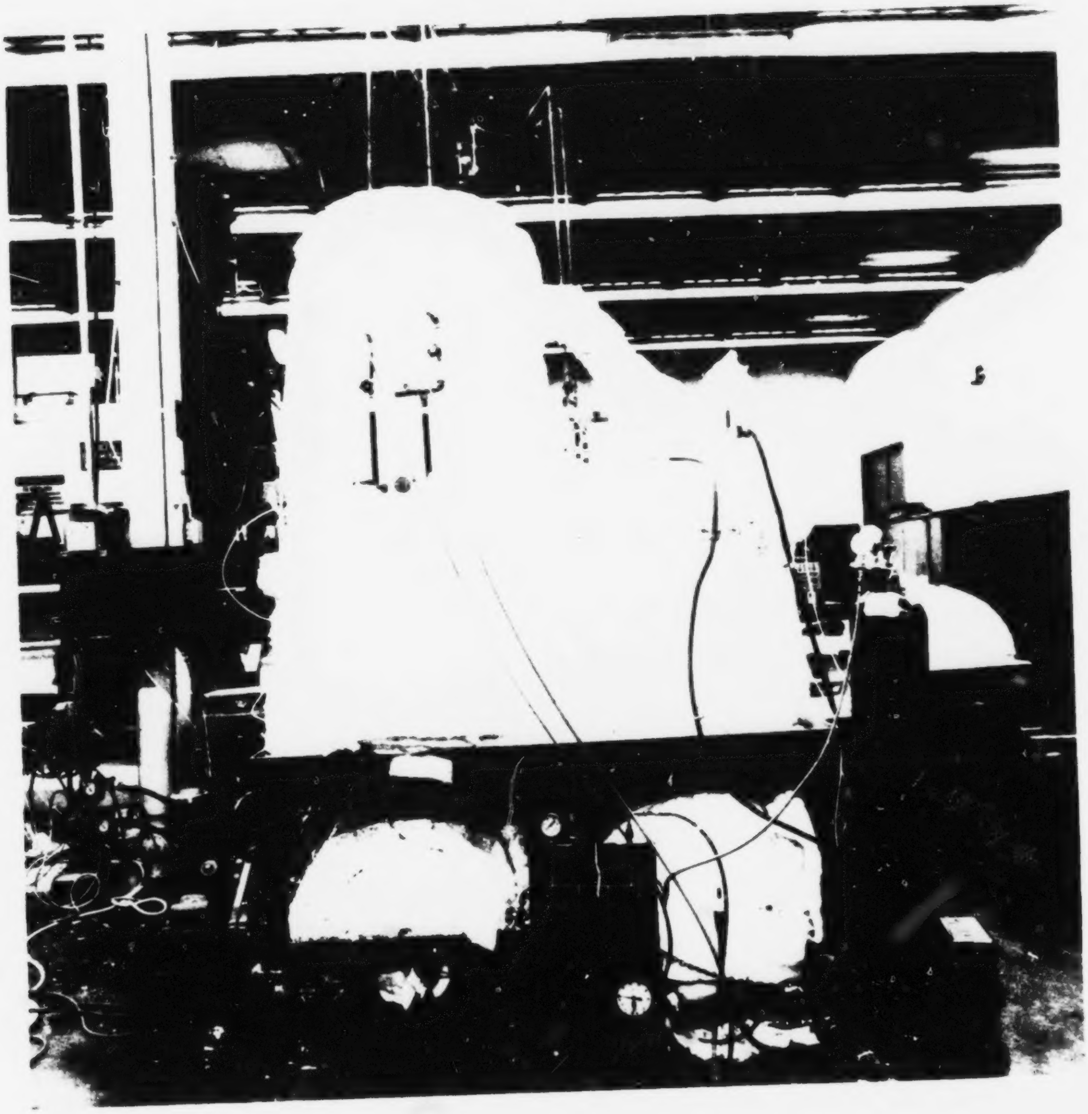

FIGURE 3 - DIRECT CONTACT HX ON-TEST

PROJECT SUMMARY

Project Title: High Temperature Integrated Thermal Storage for Solar Thermal Applications

Principal Investigators: Adam P. Bruckner and Abraham Hertzberg

Organization: Aerospace and Energetics Research Program
University of Washington
Seattle, WA 98195

Project Goals: Investigate the feasibility of an integrated high temperature solar thermal conversion and storage system based on a molten glass-like thermal storage medium and direct contact heat exchange between this medium and a working gas. Study physical and chemical properties of potential glass-like thermal energy storage materials and containment vessel materials. Investigate methods of storage material handling and transport and develop model of direct contact heat exchange between cloud of falling molten glass droplets and counterflowing gas. Develop capital, operating and maintenance cost data from a 100 MW electrical output baseline design for the proposed energy storage concept.

Project Status: The thermophysical and chemical properties of candidate glass-like thermal storage media are being investigated. A variety of silicate glasses and metal-oxide eutectics appear to show promise. Glasses containing 40-65% SiO_2 and 35-60% alkali metal oxides such as MgO, CaO and Na_2O, appear to have favorable properties such as low viscosity, low vapor pressure and low chemical reactivity with potential storage vessel refractory materials.

A parallel study of vessel materials has indicated that graphite is a very attractive refractory material for molten glass containment due to its very low reactivity, excellent thermal shock resistance, ease of manufacture and low cost. Certain composites of carbon and other refractory materials also exhibit excellent oxidation resistance and may prove useful as a liner for the solar receiver.

A numerical model of the direct contact droplet heat exchanger has been developed and is currently being used in parametric studies aimed at optimizing the baseline design to be used in the economic studies.

Contract Number: SERI XP-0-9371-1

Contract Period: April 15, 1981 - April 14, 1982

Funding Level: $51,734

Funding Source: Solar Energy Research Institute

HIGH TEMPERATURE INTEGRATED THERMAL STORAGE FOR SOLAR THERMAL APPLICATIONS

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and

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Mathematical Sciences Northwest
2755 Northup Way, Bellevue, WA 98004

ABSTRACT

A unique, high temperature (1500-2000°K) heat transfer and storage system for solar thermal applications is described. A silica-glass in bead form is melted in a solar receiver and stored in a large, refractory-lined vessel. The molten glass is available for later discharge in a direct contact droplet heat exchanger, where a working gas is heated and solid glass beads are formed for recycle. The very low cost of the storage material makes the energy related unit capital cost of this storage system an order of magnitude lower than that of the nearest competing concept.

INTRODUCTION

Efficient thermal energy storage facilities and heat transfer devices are essential for central solar energy stations if they are to be economically feasible. Few near-term power systems directly integrate energy storage. When thermal storage is provided, heat is transmitted through heat exchanger tubes or storage vessel walls. Peak temperatures are generally limited to 1000°K by materials considerations and such devices tend to be expensive.[1] The search for increased efficiency leads to higher temperatures. For example, promising power generation cycles with efficiencies ranging from 45%-70% can be achieved at peak temperatures of up to 2400°K.[2] High temperature heat transfer and storage facilities will be required for central stations based on these cycles.

We present here a unique approach in which thermal storage and heat transfer are accomplished at the same high thermodynamic potential at which the solar radiation is absorbed in the solar collector. Our approach involves a phase conversion of a refractory oxide, such as silica, which is very stable at high temperatures, to a liquid in a solar-heated furnace. This material is a very cheap substance, widely available and benign in its contact with the environment. A schematic of a proposed 100 MW solar power pilot plant which utilizes the novel heat exchanger and storage system appears in Fig. 1. The working material is delivered to the top of the solar receiver tower as a uniform aggregate of small beads, which are melted by a combination of direct solar radiation and reradiation from the cavity walls. The resulting liquid is delivered to the storage vessel and thence to the heat exchanger. The molten material is injected into the heat exchanger under pressure as small diameter streams, which break up into drops. The drops fall through a counter-flowing high pressure working gas, giving up their heat by convection and changing phase into the solid bead state in the process. The solidified droplets are collected at the bottom of the heat exchanger as an aggregate and delivered directly back to the furnace. The heated gas is removed at the top of the heat exchanger and employed by a heat engine at a temperature range corresponding to the necessary operational parameters of the system desired.

THE HEAT TRANSFER AND STORAGE MATERIAL

The heat transfer and storage material must obviously have a melting point in the range desired for an operating and storage temperature. It must also be inert at high temperature with respect to air and the working gas and should have a low vapor pressure to avoid contamination of the gas in the heat exchanger. Refractory oxides such as silica, alumina, lime, magnesia, soda, lithia, and mixtures thereof generally meet the foregoing criteria.[3] Silica has a number of attractive properties. It has a relatively low fusion point (∿2000°K), is abundant, and therefore inexpensive, and is also environmentally benign.

Although silica is very viscous in the molten state, the addition of metallic oxides such as Na_2O, K_2O, Li_2O, MgO and CaO will reduce the viscosity of a silica melt by breaking the continuity of silicate cross-linking.[4] For example, at 1725°K, the viscosity of pure silica is approximately 10^{10} poise

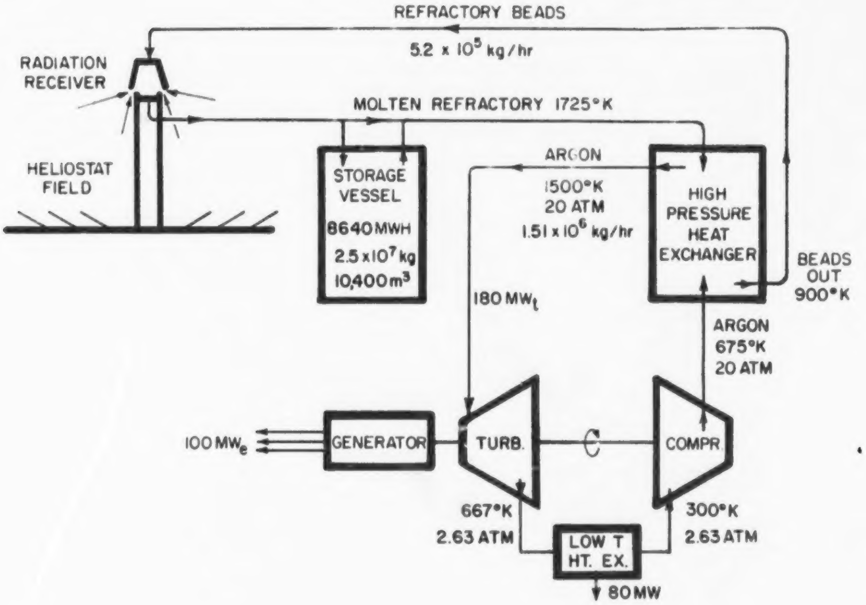
REFRACTORY BEADS
5.2 x 10⁵ kg/hr
RADIATION RECEIVER
MOLTEN REFRACTORY 1725°K
HELIOSTAT FIELD
STORAGE VESSEL
8640 MWH
2.5 x 10⁷ kg
10,400 m³
ARGON
1500°K
20 ATM
1.51 x 10⁶ kg/hr
HIGH PRESSURE HEAT EXCHANGER
BEADS OUT 900°K
180 MWt
ARGON
675°K
20 ATM
100 MWe
GENERATOR
TURB.
COMPR.
667°K
2.63 ATM
LOW T HT. EX.
300°K
2.63 ATM
80 MW

Fig. 1. Schematic of proposed high temperature solar thermal power plant.

whereas a mixture of 40% SiO_2, 20% MgO, 35% CaO and 5% Al_2O_3 has a viscosity of only 2.6 poise.[5] The additives are very stable and have low vapor pressures. The chemical reactivity of this glass melt with candidate storage vessel liner materials, such as carbon or fused-cast alumina-zirconia, is very low. A variety of other glass compositions which may have favorable properties are being investigated. There are also other possible storage materials that are being considered from the point of view of ease of handling and other potential advantages. Even common metallurgical slags and geological magmas may have properties which could be useful.

THE SOLAR CENTRAL RECEIVER

The design considerations for an optimum solar receiver geometry are only exploratory at this stage. One of several possible designs is shown in Fig. 2. The solid glass beads are delivered to the top of the receiver and fall through the solar flux as a shower of particles, to be collected as a liquid at the bottom in a refractory-lined crucible. The molten glass flows out through an aperture in the crucible at a controlled rate as a free viscous jet. The passage from the outlet of the crucible to the storage vessel at the foot of the solar collector tower consists of a large, suitable insulated refractory conduit having a diameter ∿3-4 times that of the crucible's exit aperture. In the case of loss of insolation due to a sudden overcast or nightfall, the injection of beads at the top of the solar receiver would automatically stop and the molten material in the crucible would be emptied into the storage vessel.

Preliminary considerations of the radiative coupling to the beads indicate that secondary radiative transfer from the receiver wall and/or doping the glass with an efficient absorber of solar radiation may be required to heat the beads to the desired operational temperature range (1700-2000°K). The flow of beads would be controlled to keep the melted glass in the refractory crucible at its proper maximum operating temperature.

THE ENERGY STORAGE SYSTEM

The capability of storing energy at the same high thermodynamic potential at which it is collected in the solar central receiver is a unique feature of the integrated system proposed here. Absorbing energy directly into the heat storage material in the solar central receiver leads to a storage method that is very easily integrated with the power cycle. Energy storage is accomplished by piping the molten refractory to a large storage vessel. The material fills the vessel and then proceeds to the heat exchanger tower. Thus, a reserve of high temperature molten refractory is available at all times, a feature of particular importance for solar central systems.

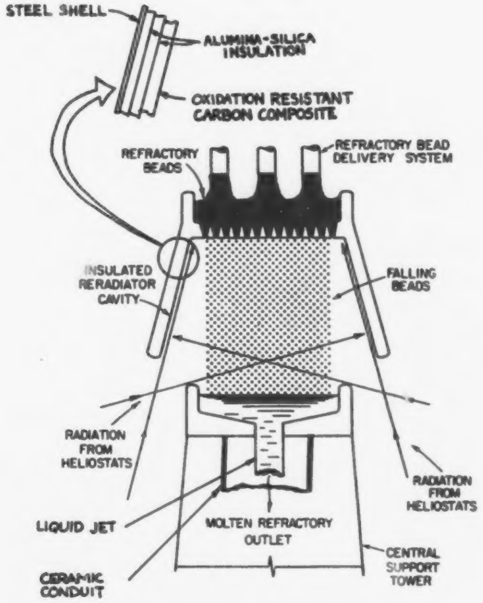
STEEL SHELL
ALUMINA-SILICA INSULATION
OXIDATION RESISTANT CARBON COMPOSITE
REFRACTORY BEADS
REFRACTORY BEAD DELIVERY SYSTEM
INSULATED RERADIATOR CAVITY
FALLING BEADS
RADIATION FROM HELIOSTATS
RADIATION FROM HELIOSTATS
LIQUID JET
MOLTEN REFRACTORY OUTLET
CENTRAL SUPPORT TOWER
CERAMIC CONDUIT

Fig. 2. Schematic of annular flux solar receiver.

The energy storage vessel, which in the point design being considered is located at ground level directly beneath the solar collecting tower, is a relatively large, unpressurized container, insulated on the inside. It is sized to hold sufficient material to supply energy to the power plant for the period it is wished to accomodate. The power plant represented in Fig. 1 has a 100 MW net ouput and requires 180 MW circulating power with the argon Brayton cycle illustrated. Storage capacity of 8640 MWH would supply the power generation cycle for 48 hours.* Silica glasses have a heat capacity of ∿0.36 cal/g°C, and a specific gravity of ∿2.4. For a temperature drop of 825°K through the droplet heat exchanger this results in a storage mass of 2.5×10^7 kg and thus a storage volume of $1.04 \times 10^4 m^3$.

The storage container must be designed with due regard for the physical and chemical stability of the liquid and the container. Much information relevant to this problem is already available from the highly developed technology of the glass industry.[3] The hot face, which is in contact with the molten storage material, could consist of fused-cast alumina-zirconia or graphitic carbon blocks. Alumina-zirconia has been developed for the sidewalls of glass-melting furnaces and is resistant both to the high temperature and the chemical attack by the molten storage material but has poor thermal shock resistance. Graphite[6] has also been used as a high temperature liner in certain applications, particularly in blast furnaces, but has not been widely used in the glass industry because of its tendency to discolor glass. However, for our purposes color purity is not a requirement and, thus, the excellent high temperature structural properties, superior thermal shock resistance, resistance to corrosion by the glass melt, ease of manufacture and low cost make graphite a very attractive liner material.[6-9]

Between the liner and the outer structural shell there would be layers of lightweight, insulating silica-alumina refractory. The roof could be constructed entirely of silica-alumina fiber refractory, since it will not be wet by the molten material. A cylindrical vessel of equal height and diameter would have a high volume-to-surface area ratio to minimize heat loss, yet be relatively easy to fabricate. Such a vessel, for the example being considered, would have inside dimensions of ∿25 m. With a suitably constructed wall 1 m thick, total heat loss could be easily kept below 1% of capacity in 48 hours.[10]

The energy-related unit capital cost estimate for the proposed molten silica storage system compares very favorably with the costs of the concepts enumerated in Ref. 11. For example, we estimate the unit capital cost of our system to be only \$3/kW-hr as compared to \$27/kW-hr for the nearest competitor - a molten salt system. The low unit cost of the silica based storage system relative to others is due primarily to the low cost of the storage material. At present we do not have the power-related costs for the molten silica system well enough defined to make a comparison, but the energy cost comparison indicates a potential for great cost savings for the molten silica system.

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*Storage capacity sufficient for 48 hours operation was chosen for the purpose of an example. There is no fundamental reason to prevent it from being sized according to individual power plant requirements.

THE DROPLET HEAT EXCHANGER

The accessibility of the stored energy to the working fluid of the energy conversion system has proved to be a problem in many of the energy storage systems considered to date.[1] The system that is proposed here allows direct contact of the stored material with a working gas at high pressure.

Engineering simplicity is also a requirement of the heat exchanger in the temperature range we are considering. Normal heat exchangers tend to consist of long passages of tubing and at best represent a complicated plumbing system subject to the potential for catastrophic single point failure. The benign nature of the glass-like storage material allows a rather unique approach which fully integrates the heat exchanger and storage system into essentially one unit.

In the system discussed here we envision a single large cylindrical pressure vessel, again insulated from the inside, as is the storage tank. A pressurized gas system would be used to force molten glass from the storage chamber through an insulated refractory pipe. The molten material is injected into the heat exchanger through a refractory nozzle plate pierced with small holes, as shown in Fig. 3. The resulting thin streams break up quickly into a series of uniform drops,[12] which fall through the heat exchanger giving up their heat to a clean working gas capable of running a high temperature heat engine.

The heat exchanger has been modeled by a simple one-dimensional flow problem. It is assumed that the refractory droplets are uniformly distributed across the flow area and are of uniform radius. The droplets are all injected at the same speed, namely, the terminal velocity in the gas at the conditions existing at the top of the tower, and the bead velocity has no radial components. The heat exchanger is a cylindrical volume with perfectly insulated sides. The gas enters at the bottom and leaves at the top with a velocity profile that is uniform across the flow area. For present purposes it is assumed that the gas velocity at the top is 50% of the droplet terminal velocity.

A computer code was generated to calculate the temperatures, heat transfer rate and gas properties through the heat exchanger for heating pressurized argon or nitrogen by molten glass droplets injected into the heat exchanger. A glass inlet temperature of 1725°K and gas inlet and exit temperatures of 675°K and 1500°K were respectively chosen to illustrate an example. The mass flow rates were adjusted to result in a constant temperature difference at all heights in the heat exchanger. Any suitable temperature difference and mass flow ratio may be chosen to tailor the temperature profiles to specific needs. The gas exit temperature is not limited by any essential part of the equipment. Higher temperatures could be achieved by choosing a particle material with a suitable melting point and designing a suitable refractory wall. Temperatures of 2000°K should be attainable with current refractory practice. Similarly, the working gas could be any species or mixture that has properties to match the power generation cycle.

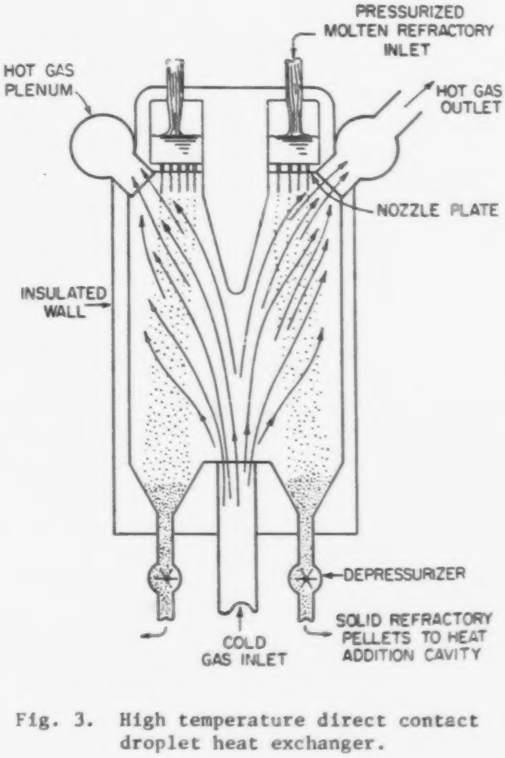
PRESSURIZED MOLTEN REFRACTORY INLET
HOT GAS PLENUM
HOT GAS OUTLET
NOZZLE PLATE
INSULATED WALL
DEPRESSURIZER
COLD GAS INLET
SOLID REFRACTORY PELLETS TO HEAT ADDITION CAVITY

Fig. 3. High temperature direct contact droplet heat exchanger.

For present purposes an argon Brayton cycle with an inlet temperature of 1500°K at 20 atm and a pressure ratio of 7.6 was chosen (Fig. 1). The cycle efficiency is 56% under these conditions. Assuming no electric generation losses, a pilot plant of 100 MW output would require 180 MW of thermal power to be delivered to the turbine inlet and would require an argon mass flow of 1.5×10^6 kg/hr and a mass flow of beads of 5.2×10^5 kg/hr.

The height of the heat exchanger is strongly dependent on the particle size, i.e., the smaller the particles, the lower the height of the heat exchanger. However, smaller particles require more injector orifices to maintain the necessary mass flow of glass. Beads of 1.5 mm dia. appear to provide a reasonable compromise. To produce droplets of this size an injector nozzle diameter of 0.71 mm is required. Injection velocity is 1.83 m/sec. The required mass flow of droplets is achieved through the use of 82,800 such nozzles spaced on a 2.1 cm grid. The injected streams of glass break up in

0.6 m, which is a small portion of the heat exchanger height. The vertical droplet spacing is ∿0.45 cm.

Transfer of the required 180 MW is accomplished in a tower 12 m high and 6.7 m dia. The beads fall through this height in 6.0 sec. Gas velocity is so low everywhere (<2 m/sec) that its momentum and kinetic energy can be neglected. The particle volume fraction is very low, $<10^{-3}$, so that the total static pressure head of gas and particles is very small. Consequently the pressure drop in the gas is less than 1% of the inlet pressure. The temperature history of the gas and the beads is shown in Fig. 4. Although the droplets solidify during their transit, the release of heat of fusion is relatively small due to the amorphous nature of the glass material and thus has not been included in the present analysis.

The parasitic losses due to injection and transport of the molten refractory in the system presented here are estimated to be <0.1% of the plant's net electrical output. The vaporization of the refractory in the heat exchanger has been calculated to be of the order of 10^{-3} kg/hr. When compared to the argon mass flow rate of 1.5×10^{6} kg/hr, it is evident that the contamination of the working gas is negligible. Similarly, the loss of working gas reresulting from removal of the solid bead aggregate at the bottom of the heat exchanger is estimated to be only ∿0.05% of the mass flow of the gas.

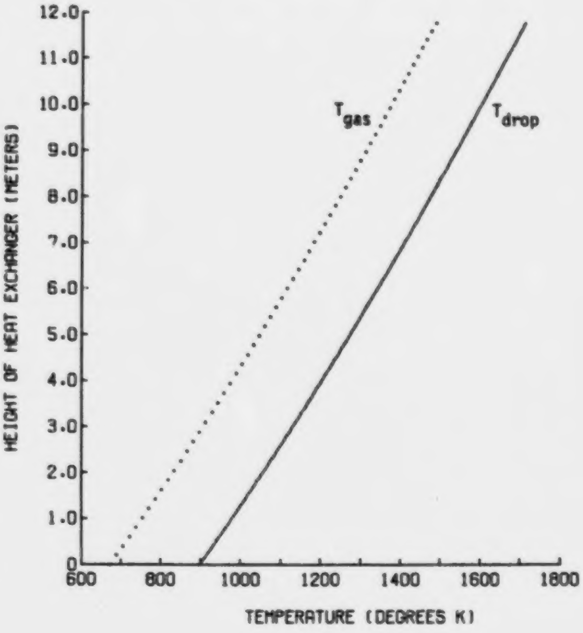

Fig. 4. Droplet heat exchanger temperature profiles.

End effects, the turbulence resulting from the presence of the cloud of beads and the interaction of the flow with the walls, will cause deviations from the simple one-dimensional flow assumed here. Collisions between beads in the area of the heat exchanger where they are still molten will result in some degree of agglomeration which will affect both the heat transfer rate and the velocity relative to the gas of the individual particles. These effects will be the subject of future investigations.

CONCLUSIONS

The high temperature thermal storage and heat transfer concepts described above will have important benefits to solar central power plants. By storing heat in a molten glass, storage costs may be reduced by an order of magnitude over the nearest competitor and the increase in efficiency of the accompanying power cycle associated with the peak temperature capabilities of the droplet heat exchanger helps to reduce the size and cost of all upstream components, i.e., heliostat field, solar receiver and thermal storage unit.

ACKNOWLEDGEMENTS

This work is supported by SERI Subcontract XP-0-9371-1.

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PROJECT SUMMARY

Project Title: New Thermal Energy Storage Concepts for Solar Thermal Applications

Principal Investigator: R. J. Petri

Organization: Institute of Gas Technology
IIT Center
Chicago, Illinois 60616

Project Goals: Assess the technical and economic feasibility of utilizing a composite latent/sensible TES media for solar thermal storage applications. Conduct composite processing and materials behavior experiments, and lab-scale TES proof-of-concept tests.

Project Status: Materials selection, composite powder processing, and media behavior tests are in progress. Future work includes TES module assembly and performance testing of most promising media, and assessment of overall technoeconomic feasibility.

Contract Number: SERI XP-0-9371-2

Contract Period: June 15, 1981 through April 15, 1982

Funding Level: $59,779

Funding Source: U.S. Department of Energy through Solar Energy Research Institute

HIGH-TEMPERATURE COMPOSITE LATENT/SENSIBLE HEAT STORAGE

T. D. Claar R. J. Petri
Institute of Gas Technology
IIT Center
Chicago, Illinois 60616

ABSTRACT

A composite latent/sensible media concept is being evaluated for technical and economic feasibility of satisfying high-temperature solar thermal energy storage requirements. The approaches being taken to identify and resolve critical technical issues associated with this advanced TES concept are discussed.

INTRODUCTION

Numerous thermal energy storage technologies are under development for application in solar thermal power systems to provide for continuous operation during nonsolar hours and during periods of variable insolation, as outlined in Reference 1. First-generation TES subsystems include dual media oil/rocks and oil thermoclines. Second-generation TES technology development is focusing on storage subsystems for solar receivers cooled by water/steam, molten salts, liquid metals, organic fluids, or gases. The objective of the current effort is to investigate the technoeconomic feasibility of an advanced TES media concept that offers potential cost/performance benefits over second-generation solar Brayton TES technologies and that will provide an advanced TES technology base for application in future solar thermal systems.

COMPOSITE LATENT/SENSIBLE MEDIA CONCEPT

A number of technology development and systems studies have been conducted on latent-heat storage using inorganic salt phase-change materials (PCM) (e.g. carbonates, chlorides, fluorides, hydroxides, and nitrates). In general, the results of these efforts have shown the advantages of latent-heat systems in providing high energy storage densities and availability of stored latent heat at constant temperature. Most efforts have focused on containment of molten salts in a shell-and-tube HX configuration. However, passive tube-intensive designs have inherent heat transfer performance limitations caused by growth of solid salt layers on external HX tube surfaces during thermal discharge. Attempts to improve thermal performance through use of high-conductivity extended surfaces and active concepts using mechanical salt scrapers have met with limited success. Another drawback of tube-intensive latent heat designs is that systems for very-high-temperature (>700°C) applications, require the use of superalloy HX tube materials for adequate strength and corrosion resistance, significantly increasing capital costs.

The objective of the current study is to assess the potential of an advanced media concept which takes advantage of the attractive properties of phase-change materials, while eliminating the performance and cost limitations associated with tube-intensive systems.

This novel composite media concept involves retention and immobilization of phase-change salts within porous ceramic matrices.* The ceramic phase may consist of a distribution of discrete submicron sized particles, as shown in the schematic microstructure of Figure 1, or as an interconnected phase in a partially sintered porous body. The molten salt is retained within the void space defined by the ceramic network, primarily by capillary forces. The volume fraction of molten salt that can be retained is determined by characteristics of the support material (particle size and shape, distributions, specific surface area), salt properties (surface tension, viscosity), and wetting behavior between molten salt and ceramic. The feasiblity of retaining 65 vol % molten alkali carbonates within a ceramic particle matrix at 700°C has been experimentally demonstrated. Retention of higher volume fractions of liquid is possible by optimization of ceramic support characteristics and media processing conditions.

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* IGT has filed a patent application on this concept.

BEST DOCUMENT AVAILABLE

Immobilization of the latent-heat PCM phase within the ceramic support structure, which provides a sensible-heat contribution, will permit operation of composite pellets, bricks, or other shapes in direct contact with compatible fluids and elimination of costly HX tubes. Higher heat transfer rates are expected due to both control and minimization of solidified salt thicknesses and elimination of thermal resistances associated with heat exchanger tubes. Media shapes and sizes can be readily varied to optimize heat transfer surface/volume ratio and bed packing density.

The technical feasibility of this approach will depend on a number of key factors:

- Ability of the ceramic support to retain adequate amounts of molten salt by capillary action, with minimal chemical interaction between salt and ceramic. Creepage of molten salt from the porous shape must be minimal.

- Ability of the salt/ceramic composite to be repeatedly thermal cycled (melting/solidification of the salt phase) with minimal cracking, spalling, or other structural damage.

- Chemical compatibility of the molten salts with solar TES charge/discharge fluids to minimize vaporization losses or changes in salt chemistry, melting behavior, surface tension, and other critical physical properties.

- Sufficient strength to maintain physical integrity under the stresses imposed by the system design.

MEDIA DEVELOPMENT AND FEASIBILITY STUDIES

One possible solar application of the concept is in storage for solar Brayton power systems operating at 700° to 900°C with air or helium working fluids. Mixtures of alkali metal/alkaline earth metal carbonates have been selected for development and evaluation based on the availability of moderate-cost carbonate compositions with melting temperatures in this range, and their high-temperature thermochemical stabilities in both inert and oxidizing environments. Ceramic support materials are being selected from among metal oxides and aluminates. Figure 2 shows enthalpy curves for several candidate latent- and sensible-heat materials.

In keeping with the high-temperature requirements of solar Brayton systems and the desirability of minimizing media costs, emphasis is being given to carbonate compositions based on Na_2CO_3. Sodium carbonate melts at 858°C with a heat-of-fusion of 114 Btu/lb and costs $0.03/lb as a technical-grade salt. Other available high-melting compositions include 48 wt % Na_2CO_3-52 wt % $BaCO_3$ (686°C m.p.) and 50 wt % Na_2CO_3-50 wt % K_2CO_3 (710°C m.p.). In addition, the Na_2CO_3-K_2CO_3 phase diagram indicates a complete range of solid solutions, providing for some modification of thermal and physical properties by varying composition in this system.

The development and evaluation studies under this program are summarized as follows:

- Composite Media Preparation

Composite carbonate/ceramic powders are prepared by spray drying aqueous slurries containing the appropriate raw materials, followed by high-temperature calcining. Spray drying and calcining process conditions are systematically varied to establish procedures that yield satisfactory powders for forming functional TES media. Composite media pellets are formed by cold-pressing the powders in steel dies and heating above the carbonate melting point. Initial studies are focusing on processing and stability of Na_2CO_3 and Na_2CO_3-$BaCO_3$ salts containing low-cost, commercially available MgO supports and Na_2CO_3-$BaCO_3$ compositions supported by $NaAlO_2$ particles. Available data presented in References 2-4 indicate that $NaAlO_2$ is less soluble than MgO in molten carbonates, and thus may have greater long-term resistance to particle coarsening in this application. Figure 3 shows pellets of Na_2CO_3-$BaCO_3$ supported by $NaAlO_2$ particles after heating at 850°C for 50 hours, prepared under this program.

In addition, the results of an on-going program (ORNL/UCC Subcontract No. 86X-9500-1C) focusing on industrial applications of this advanced media concept are being made available to this solar TES program. This information will include processing and materials stability data for other ceramic support materials in Na_2CO_3 and Na_2CO_3-based mixtures, and fabrication techniques for mass production of media pellets.

- Evaluation of Composite Media Behavior

The candidate composite media are being evaluated in experiments designed to address and quantify key technical issues expected to significantly influence their functionality under solar thermal storage conditions. These tests include thermogravimetric analysis to evaluate salt decomposition and vaporization loss effects in proposed solar Brayton working fluids (air and helium), and thermal aging and thermal cycling tests for measuring support particle stability, carbonate retention, and media thermal shock resistance and shape dimensional stability.

- Proof-of-Concept TES Testing

The most promising materials and processing techniques will be utilized in laboratory-scale TES charge/discharge testing of the concept. Composite pellets will be thermally charged and discharged in direct contact with proposed solar Brayton working fluids. Pertinent system cycling characteristics (heat transfer rates, efficiency, pressure drops, etc.) will be monitored to provide the data base required to assess overall concept feasibility. Post-test media examinations will be performed to determine the effects of thermal cycling and exposure to high-temperature gases on composite materials stability.

- Performance and Economic Analysis

Preliminary analyses indicate that a direct contact TES subsystem containing composite carbonate/ceramic media offers potential cost and performance advantages over proposed second-generation solar Brayton storage concepts utilizing MgO or Al_2O_3 refractory sensible-heat media. The lab-scale TES performance data and media stability results will be analyzed to improve and expand these initial cost and performance benefits.

CONCLUSION

The results of media development and lab-scale TES testing activities will provide the data base required for assessing the technical and economic feasibility of this direct-contact latent/sensible media concept for solar thermal storage applications. Needs for further technology development and systems analysis will be identified.

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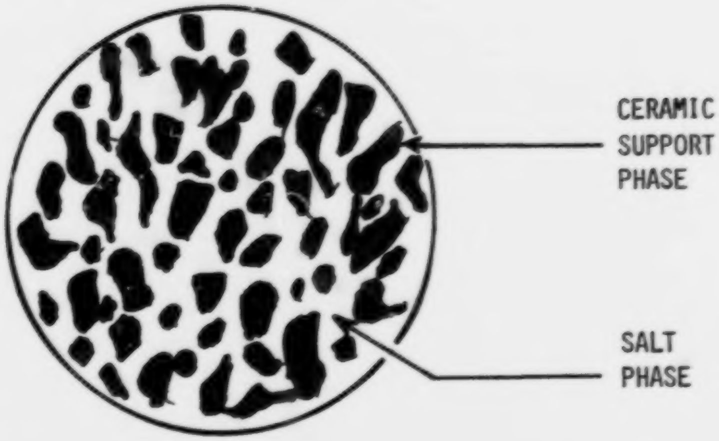
CERAMIC SUPPORT PHASE
SALT PHASE

Fig. 1. Schematic Microstructure of Composite TES Media: Molten Salt Supported by Ceramic Matrix

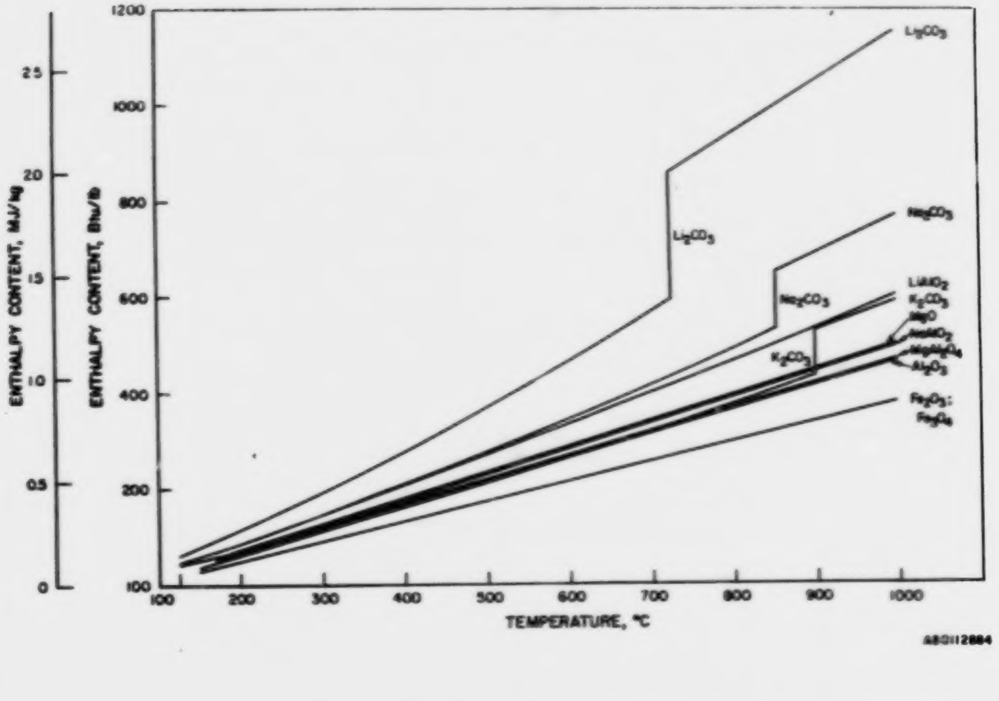

Fig. 2. Enthalpy Contents of Selected Sensible- and Latent-Heat Storage Materials

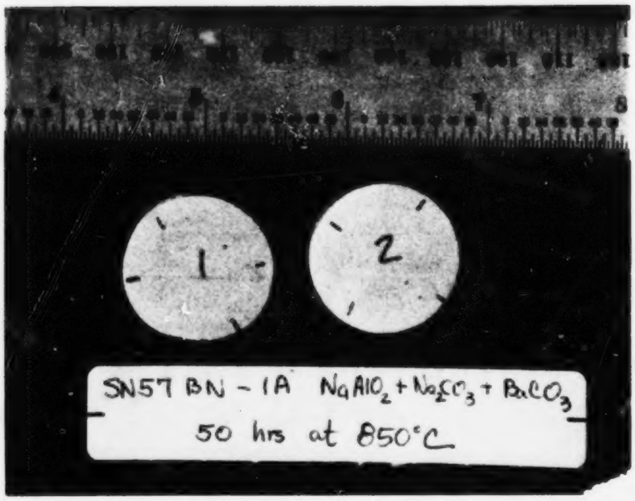
8
1
2
SN57 BN - 1A $NaAlO_2 + Na_2CO_3 + BaCO_3$
50 hrs at 850°C

Fig. 3. Composite Pellets of Na_2CO_3-$BaCO_3$/$NaAlO_2$ Particulates After Cold-Pressing and Heating at 850°C for 50 Hours

THE THERMAL and CHEMICAL STORAGE ANNUAL CONTRACTORS' REVIEW MEETING

Washington, D.C.
September 14-16, 1981

UNITED STATES DEPARTMENT OF ENERGY
OFFICE OF ENERGY SYSTEMS RESEARCH, DIVISION OF
PHYSICAL AND CHEMICAL ENERGY STORAGE

Coordinated by Oak Ridge National Laboratory
Meeting Moderator: James F. Martin

AGENDA

SUNDAY, SEPTEMBER 13, 1981

6:00 - 9:00 pm	Registration/Reception (Grand Ballroom - Salon E)

MONDAY, SEPTEMBER 14, 1981

8:00 - 9:00 am	Registration (Continued) - Ballroom Foyer
8:00 - 9:00 am	Continental Breakfast - Ballroom Foyer
8:00 - 9:00 am	Review Committee Meeting (McLean Room)

THERMAL AND CHEMICAL STORAGE REVIEW MEETING

(Grand Ballroom - Salons E & F)

9:00 - 9:15 am	Agenda, Announcements, General Information	J.F. Martin (ORNL)
	Introductory Remarks	Headquarters Staff DOE

SESSION I BROOKHAVEN NATIONAL LABORATORY CHEMICAL/HYDROGEN ENERGY SYSTEMS

9:15 - 9:35 am	Program Overview	A. Mezzina (BNL) Moderator

HYDROGEN PRODUCTION (Electrolytic)

9:35 - 9:55 am	Solid Polymer Electrolyzer	J.H. Russell (G.E.)
9:55 - 10:15 am	Advanced Alkaline Water Electrolysis	J.N. Murray (Teledyne)
10:15 - 10:35 am	Static Feed Water Electrolysis	F. Schubert (Life Systems)
10:35 - 11:00 am	COFFEE BREAK (Ballroom Foyer)	

For information: MCC Associates, Inc., 8534 2nd Avenue, Silver Spring, Md. 20910 (301) 589-8130

11:00 - 11:20 am	Electrode Materials Evaluation	G. Stoner (U. of Va.)
11:20 - 11:40 am	Electrolyzer Technology Evaluation	J. Parry (A.D. Little)
11:40 - 1:00 pm	LUNCHEON (RAFFLES LOUNGE)	
1:00 - 1:20 pm	Advanced Electrochemical Support Activity	J. McBreen (BNL)

HYDROGEN PRODUCTION (Thermochemical)

1:20 - 1:40 pm	Thermochemical Water Splitting Program	G. Besenbruch (General Atomic)
1:40 - 2:00 pm	Alternate Thermochemical Cycles	C.M. Hollabaugh (LANL)
2:00 - 2:20 pm	Thermochemical Research	L. Compton (JPL)
2:20 pm	BNL CHEMICAL ENERGY SYSTEMS	C.P. Fredrickson (BNL) Moderator

HYDROGEN STORAGE/RECOVERY

2:20 - 2:40 pm	Hydrogen Compatibility of Steels	J. Holbrook (Battelle/Columbus)
2:40 - 3:00 pm	COFFEE BREAK (Ballroom Foyer)	
3:00 - 3:20 pm	Hydrogen Purification/Separation	L. Huston (Ergenics)
3:20 - 3:40 pm	Recovery of Hydrogen from Hydrogen Sulfide	G. Krishnan (SRI)
3:40 - 4:00 pm	Systems Analysis of H_2/Natural Gas Supplementation & Separation	M. Beller (BNL)
4:00 - 4:20 pm	Hydrogen Recovery from Supplemented Natural Gas	F. Hill (BNL)

CHEMICAL HEATPUMP

4:20 - 4:40 pm	Sulfuric Acid/H_2O CHP	E.C. Clark (Rocket Research)
4:40 - 5:00 pm	CHP Cost Effectiveness Evaluation	W. Standley (TRW)

TUESDAY, SEPTEMBER 15, 1981 (Grand Ballroom - Salons E & F)

7:45 - 8:30 am	Continental Breakfast (Ballroom Foyer)	

BNL CHEMICAL ENERGY SYSTEMS (Continued)

8:30 - 8:50 am	Metal Hydride CHP Development	H. Madariaga (So. Ca. Gas)

8:50 - 9:10 am	Metal Hydride CHP Analytical Support	H. Abelson (ANL)
SESSION II	OAK RIDGE NATIONAL LABORATORY THERMAL ENERGY STORAGE (TES) FOR BUILDING HEATING AND COOLING, AND INDUSTRIAL APPLICATIONS	
9:10 - 9:30 am	Program Overview	J.F. Martin (ORNL)
	TES FOR BUILDING HEATING & COOLING	J.J. Tomlinson (ORNL) Moderator
	Utility Load Management Application	
9:30 - 9:50 am	Evaluation of Latent TES and Heat Pump System	T.W. Sigmon (RTI)
9:50 - 10:10 am	Residential Scale Ice Storage System for Space Cooling	H.H. Hopkinson (Carrier)
10:10 - 10:30 am	Evaluation of Olivine Refractories for TES	B.M. Gay (NCSU)
10:30 - 10:50 am	COFFEE BREAK (Ballroom Foyer)	
10:50 - 11:10 am	Alternatives to Ceramic Bricks and Ceramic Brick Systems	J.M. MacDonald (TRW)
11:10 - 11:30 am	Assessment of Cool Storage for Commercial Buildings Applications	J.G. Asbury (ANL)
	Solar Applications	
11:30 - 11:50 pm	Pelletization and Roll-Encapsulation of PCMs	J.C.H. Chen (Pennwalt)
11:50 - 1:20 pm	LUNCHEON (on your own)	
1:20 - 1:40 pm	Effect of Additives on Performance of Hydrated Salt TES Systems	C.D. MacCracken (Calmac)
1:40 - 1:50 pm	PCMs in Building Materials for Passive Solar	J.J. Tomlinson (ORNL)
1:50 - 2:10 pm	Assessment of Energy Storage for Solar Applications	D.J. Edwards (Aerospace)
	Conservation Applications	
2:10 - 2:30 pm	Commercial TES Installations in the U.S. and Canada	H.G. Lorsch (Franklin)
2:30 - 2:50 pm	Performance of Labyrinth-Stratified Water Storage System	M.W. Wildin (U. of NM)
2:50 - 3:10 pm	COFFEE BREAK (Ballroom Foyer)	
3:10 - 3:30 pm	Development of Natural Stratification Technology	F.O. Bellinger (ANL)

3:30 - 3:50 pm	Program Technical Support	R.N. McGill (ORNL)
	TES FOR INDUSTRIAL APPLICATIONS	M. Olszewski (ORNL) Moderator
3:50 - 4:10 pm	Heat Exchanger Development and Evaluation	L.B. Katter (Rocket Research)
4:10 - 4:30 pm	Development and Evaluation of Advanced TES Concepts for District Heating Applications	G.L. Vanroyen (Trans Energy)
6:30 - 7:30 pm	CASH BAR RECEPTION (Salons A & B)	
	Poster Display	
7:30 - 9:30 pm	BANQUET (Salons C & D) Congressional Perspectives on Energy Research and Development	Ezra Heitowit (House Committee on Science & Tech)

WEDNESDAY, SEPTEMBER 16, 1981 (Salons E & F)

7:45 - 8:30 am	Continental Breakfast (Ballroom Foyer)	
8:30 am	ORNL TES FOR BUILDING HEATING AND COOLING, AND INDUSTRIAL APPLICATIONS (Continued)	
8:30 - 8:50 am	TES Technology Transfer in the Pulp and Paper Industry	H. Edde (H. Edde, Inc.)
8:50 - 9:10 am	R&D for Advanced Carbonate Salt TES Systems for Industrial Applications	R. Waibel (IGT)

SESSION III SANDIA NATIONAL LABORATORY SOLAR THERMAL APPLICATIONS

9:10 - 9:30 am	Solar Thermal Applications Overview	W.G. Wilson (SNL) Moderator
9:30 - 9:50 am	Molten Nitrate Salt Studies for Central Receiver Applications	S. Goods (SNL)
9:50 - 10:10 am	Molten Salt Thermal Energy Storage Subsystem Research Experiment	P. Wells (Martin Marietta)
10:10 - 10:30 am	Effects on Soils from Hot Storage Tanks	K. Ko (K. Ko & Assoc.)
10:30 - 10:50 am	COFFEE BREAK (Ballroom Foyer)	
10:50 - 11:10 am	Moving Bed Thermal Energy Storage for High Temperature Applications	R. Wright (Babcock & Wilcox)
11:10 - 11:30 am	Latent Heat Storage for Saturated Steam Receivers	G. di Lauro (Combustion Eng.)

11:30 - 11:50 am	Status Report of Thermocline Thermal Energy Storage Studies at Sandia	R. Gross (SNL)
11:50 - 1:20 pm	LUNCHEON (on your own)	
1:20 - 1:40 am	Dish Mounted Latent Heat Buffer Storage	R. Manvi (JPL)
1:40 - 2:00 am	Storage Requirements Definition and SRE Design for Dish Brayton Systems	H.J. Strumpf (AiResearch)

SESSION IV SOLAR ENERGY RESEARCH INSTITUTE - RESEARCH & DEVELOPMENT AND ANALYSIS & ASSESSMENTS

2:00 - 2:20 pm	An Overview of the SERI Solar Energy Storage Program	C.E. Wyman (SERI) Moderator
2:20 - 2:40 pm	Cost and Performance of Thermal Energy Storage for Solar Thermal Applications	A.W. McKenzie (Stearns-Roger)
2:40 - 3:00 pm	Systems Analysis of Thermal Storage	R.J. Copeland (SERI)
3:00 - 3:20 pm	COFFEE BREAK (Ballroom Foyer)	
3:20 - 3:40 pm	Thermochemical Energy Storage and Transport Research	R. G. Nix (SERI)
3:40 - 4:00 pm	High Temperature Active Heat Exchanger Research for Latent Heat Storage	J. Alario (Grumman)
4:00 - 4:20 pm	High Temperature Integrated Thermal Storage for Solar Thermal Applications	R.T. Taussig (U. of Wa.)
4:20 - 4:40 pm	High Temperature Composite Sensible/Latent Heat Storage	T.D. Claar (IGT)

THURSDAY, SEPTEMBER 17, 1981 (McLean Room)

9:00 - 12:00 am Executive Session/Review Committee Report

THE THERMAL and CHEMICAL STORAGE ANNUAL CONTRACTORS' REVIEW MEETING

Washington, D.C.
September 14-16, 1981

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